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PROCEEDINGS  
OF THE  
AMERICAN ACADEMY  
OF  
ARTS AND SCIENCES.  
VOL. XXI.

PAPERS READ BEFORE THE ACADEMY.

INVESTIGATIONS ON LIGHT AND HEAT, MADE AND PUBLISHED WHOLLY OR IN PART WITH  
APPROPRIATION FROM THE RUMFORD FUND.

I.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XX.—ON THE EFFECT OF TEMPERATURE ON THE  
VISCOSITY OF AIR.

BY SILAS W. HOLMAN.

Communicated May 13, 1885.

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Apparatus, Description of . . . . .	2	Critique of the Method, including Compar-	
Procedure in Measurements . . . . .	6	isons of Mercurial and Air Thermome-	
Experimental Results . . . . .	7	ters . . . . .	25
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Air and CO <sub>2</sub> . . . . .	19		

THE investigation described in the present paper is a continuation of the work done on the same subject by the author in 1876.\* The experimental portion of the work consists of about 250 independent measurements of the viscosity of air and 140 of carbon dioxide (carbonic acid), besides somewhat extended incidental researches on thermometry. The temperature ranges for air were from 0° to 124° C.; for carbonic acid, from 0° to 225° C. The plan adopted at the outset was to make some study of the method and of the best form of apparatus; then to proceed to the study of several gases which have been

\* On the Effect of Temperature on the Viscosity of Air, Proc. Amer. Acad. Arts and Sci., xii. (1876), p. 41. Phil. Mag., iii. 81 (1876). Wied. Beibl., i. 222.

already well investigated, either in regard to their viscosity or other properties, making measurements of the viscosity at temperature intervals of about  $20^{\circ}$  from low to high temperatures. But the laborious nature of the observations, and the large amount of time demanded by the observations and their reduction, have rendered the fulfilment of the plan impossible for one whose available time has been fully occupied with laboratory instruction. It will be seen that the last of the observations given were made in April, 1880. Since that date it has been wholly inconsistent with the author's duties and health to continue the work, and the incomplete results are now presented in the hope that, despite their limited range, they may be a contribution of some permanent value to the subject treated.

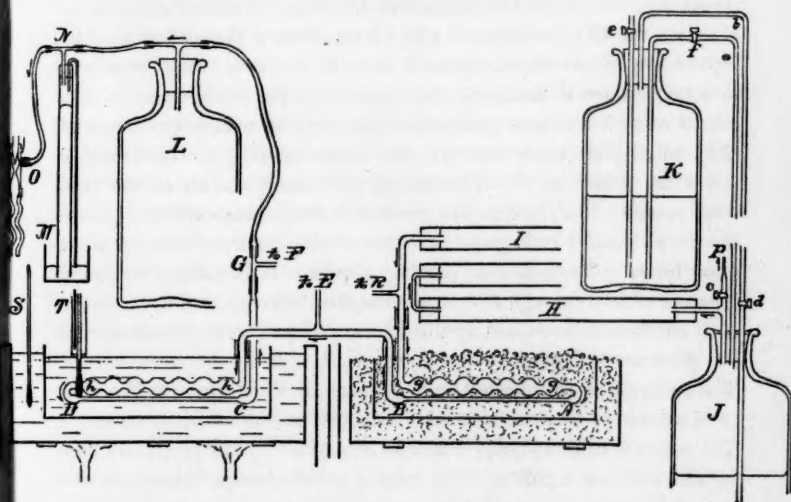
The expenses of the investigation have been mainly defrayed by an appropriation granted by the American Academy of Arts and Sciences from the Rumford Fund for researches on Light and Heat.

The objects of the investigation were concisely stated in the paper of 1876. The extension of the work was looked to for the development of data which not only should furnish another experimental check on the deductions of the kinetic theory of gases, but should provide material of sufficient precision (approximating to that with which the coefficient of expansion of gases is known) to serve as a part of that experimental basis on which the complete theory of gases, and indeed of molecular physics in general, must eventually rest. The critical review of the method, given at the end of the paper, is intended to furnish the material for the formation of a judgment as to how far this object has been fulfilled in the case of the gases investigated.

#### APPARATUS.

The apparatus used is shown in the schematic section given by the accompanying cut. It is in principle the same as that used in the former measurements. The dried gas is transpired successively through two glass capillaries of about 30 cm. in length, from a space containing the gas at a measured pressure to another space from which the gas is continuously exhausted as fast as it enters, and which is thus maintained at a constant and measured pressure. The pressure of the gas in the intermediate space is also measured. The capillaries are maintained at known or measured constant temperatures, *AB* being usually packed in finely pounded ice, and *DC* being in a jacketed double oil-bath, of which the temperature is maintained nearly constant by regulating the flame of the gas-burners, and is measured by the thermometer with its

bulb at *D*, the entrance to the capillary. Both inner and outer oil baths are continuously stirred by an agitator moved to and fro through the troughs by a water motor with connections not shown in the sketch. This arrangement maintained temperatures as high as  $225^{\circ}$  constant within about  $0.5$  in most measurements, and so nearly uniform throughout the trough that no perceptible difference could be found at various points along the capillary. A thermometer at *S* in the outer bath served to adjust the lamps so that their heating should be such as to maintain a nearly constant temperature. Automatic thermo-regulators were tried, but were found in general to be quite as much of a disadvantage as benefit, and were abandoned.



The details of the apparatus will be described, beginning at the point where the gas enters. When air was used, the laboratory air was drawn in through caustic potash to remove the carbonic acid, and through concentrated sulphuric acid, fused chloride of calcium, and anhydrous phosphoric acid in the tubes *H* and *I*, which are further described at I. 2, p. 29. When carbonic acid was used, the gas was formed by the action of hydrochloric acid on marble, was purified by washing in water, dried, and freed from hydrochloric acid by passing through tubes of pumice coated with anhydrous copper sulphate. The gas was then drawn through *P* into *J* by withdrawing the concentrated sulphuric acid from *J* into *K*, as about to be described, and was there held for use. When a measurement was in progress, the gas in *J*, being

slowly and uniformly displaced by the sulphuric acid returning from *K*, passed into and through *H* and *I*, arranged as already described. The glass bottles *J* and *K* held each about 10 litres, and one was filled with concentrated sulphuric acid. *K* was placed about a meter above *J*. The two were connected by two glass tubes, *a* and *b*, each containing a stop-cock, and had other tubes arranged as shown in the sketch. To withdraw the sulphuric acid from *J* into *K*, and to replace this by the  $\text{CO}_2$ , it was necessary simply to connect *P* to the gas-holder or generator, to close *e* and *f*, to open *c*, to exhaust the air from *K* by an aspirator, and, opening the cock in *b*, to allow the  $\text{H}_2\text{SO}_4$  to be transferred to any desired extent. This being accomplished, *d* and *c* were closed and the generator disconnected. When a measurement is in progress, the  $\text{CO}_2$  passing at a uniform rate from *J* through *Q* must be replaced by sulphuric acid from *K* through *a*. This flow is regulated by a tangent screw motion on the cock *f*, until the liquid drops or runs into *J* at such a rate as to displace not only the necessary amount of  $\text{CO}_2$ , but slightly more than this, the excess escaping slowly through *c* and a fine orifice at *P*. This arrangement maintains an almost constant pressure in *J*, and, as the pressure is thus always outward, there can be no inward leakage of air either during the measurements or at other times. The gas, after passing, always with this slight excess of pressure within, through *HI*, enters the glass bulbs *gg*, and the pressure  $p_1$  at entrance is measured by the barometric height at the time plus the pressure indicated by the gauge at *R*, read by the cathetometer. The bulbs *gg* were spherical enlargements of about three centimeters in diameter of a glass tube of about half a centimeter in diameter. The contents of these bulbs would be transpired by the capillaries once in about fifteen minutes. The tube *gg* and the capillary were connected into one piece at *A* by melting them together, and a similar solid connection was made at *B* to an exit tube. The tubes *CD* and *hh* were similar in all respects to *AB* and *gg*, the capillaries being of very nearly the same length, and cut from the same piece of tubing, which was one of those used in the experiments of 1876. The connections of these tubes to the other tubing of the apparatus, as shown in the drawing, were all made as described in I. 3, p. 29. The tube connecting *B* to *hh* was of about 3 mm. internal diameter and 50 cm. length, and at its middle point contained a branch, which extended, with one joint of the kind described, to the gauge *E*, which in connection with the barometer served to measure  $p_2$ . The gas at exit from *C* passed about 50 cm. of 3 mm. tubing to the point *G*, where a side branch led to the gauge *F*, which gave the pressure  $p_3$ . Passing by *G*,

the gas moved forward past *N* to the aspirator *O*,\* and then escaped. The bottle *L*, of about 10 litres' capacity, sometimes two bottles each of that volume, connected between *G* and *N*, served to reduce the rate of pressure fluctuations arising from irregularities in the aspiration. At *N* was connected the pressure-regulator, which I will describe in detail, as it is so far as I know wholly new and is available for many purposes.

The aspirator under a given head of water can exhaust at a definite rate, maintaining a certain exhaustion; if the head be increased or lessened, the rate of exhaustion will be increased or diminished, and thus if the leakage into the exhausted space, as through the capillaries in this case, be sensibly constant, the pressure in the exhausted space must diminish or increase. It is often impracticable, as it was for me, to maintain a constant head of water, and some means is therefore necessary to overcome this irregular action. The arrangement used was that shown in the sketch. A large glass tube *M*, open at both ends, stands upright in an open mercury trough of considerably larger dimensions. Into its top is inserted a rubber stopper with two borings, through one of which passes one arm of a T joint whose other two arms are connected respectively with the aspirator and the vessel to be exhausted. Through the other boring passes a tube of 1 mm. to 2 mm. diameter bent twice at right angles, and dipping into the mercury in the trough. Suppose that the vessel to be exhausted is closed — the apparatus covers cases ranging from this to a leakage of about half the rate of exhaustion of which the pump is capable — and the aspirator set in operation. As the exhaustion proceeds, the mercury rises equally in both large and small tubes until the mercury in the trough drops below the point of the latter, whereupon, as soon as the excess of external pressure is sufficiently great to overcome the friction of the mercury, the column in the fine tube rises rapidly and flows over into the upper part of the large tube and upon the mercury surface in it. This overflow is of course immediately followed by an inrush of air through the open point, and a consequent sudden lowering of the mercury in the large tube with a corresponding rise of level in the trough which closes or partly closes *D*. This first sudden action is followed by several of lessening violence, and a steady condition is soon reached, in which there is a continuous inflow of air and small drops of mercury at the point, the

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\* Richard's jet aspirator was used. See Amer. Jour. Sci., [3], viii. 200; Chem. News, xxxiv. 141; Trans. Amer. Inst. Mining Eng., vi. 492 (1879).

proportion between the two depending upon the relation between the sizes of the tubes, the capacity of the aspirator, and the supply of gas from the vessel to be exhausted. If a fluctuation occurs in either the rate of the aspiration or the supply of gas to be exhausted, a greater or less proportion of air will be taken in, with a corresponding but very small change of the pressure within the apparatus. For the successful working of the apparatus a proper proportioning of parts to the work to be done is of course necessary, and this is mainly to be accomplished by varying the size of the point to which the fine tube is drawn out. The sensitiveness of the apparatus may be increased by using a *U* tube, instead of a vertical straight tube with cistern, and allowing the fine tube to extend into the open arm of this tube. A stricture at some point of the *U* reduces the too sudden fluctuations. Various other modifications will readily suggest themselves to persons using the apparatus. The regulator is of course of service in other ways than merely rendering uniform the action of the aspirator. It is possible to maintain with it a constant exhaustion of any desired amount up to the full exhaustion which the aspirator can produce when working under the smallest head of water likely to occur; and in the form of a *U* tube, with various lengths of tube *DE*, to be inserted at *A* and raised or lowered, it affords a very convenient means of varying the exhaustion at will.

#### PROCEDURE IN MEASUREMENTS.

The first operation is thoroughly to dry the apparatus and fill it with pure dry gas. This was accomplished by repeated exhaustion and refilling of all necessary parts of the tubing, gauges, etc., none but thoroughly dry gas being admitted. This operation was repeated on each separate day of measurement so that any error from slight leakage or diffusion of either air or moisture should be avoided. On the first introduction of the dry air or carbonic acid, the further precaution was taken to run the apparatus under quite high exhaustion for many hours consecutively; and in all cases, on each day of measurement, the apparatus was run for an hour or more before any readings were taken.

The procedure in measurement was as follows. The aspirator was set in operation, *J* being full of the gas. The generator and purifiers were connected at *P*, and the cock *c* opened, *f* remaining closed, so that the supply of gas came from the generator; the temperature of *DC* was regulated, the stirrer being in continuous operation; the ice-bath

was placed around  $AB$ , the regulator at  $N$  adjusted, and the transpiration allowed to proceed until the gauges  $E$  and  $F$  were nearly stationary. Then  $c$  was closed, and  $f$  opened and adjusted so that the reading of  $R$  slowly increased, whereupon  $c$  was again opened for the slow escape of the gas and the maintenance of a constant initial pressure  $p_1$ . The transpiration was allowed to proceed until  $E$ ,  $F$ , and  $R$  were sufficiently near stationary, when readings of the mercury columns by the cathetometer and of the thermometers were taken systematically. After a complete set of readings had been thus obtained, the apparatus was thoroughly inspected and a second set made; and so on until the number was deemed sufficient, whereupon the temperature of  $DC$  was changed or the pressure modified as desired. The results thus obtained furnished, on reduction, the values of  $p_1$ ,  $p_2$ ,  $p_3$ , and  $t$  for the computation of the ratio of the coefficient of viscosity at the higher temperature to that at  $0^\circ \text{C.}$ , the further requirements being the constants  $\frac{R_2^4 \lambda_1}{R_1^4 \lambda_2} = K$  for the tubes,  $R_1$  and  $\lambda_1$ ,  $R_2$  and  $\lambda_2$ , being the radius and length respectively of the tubes  $AB$  and  $CD$ , as shown at page 9. This value of  $K$  was found from measurements similar in all respects to those just described, except that the tubes  $AB$  and  $CD$  were both surrounded with ice at the same time.

The apparatus was also arranged to place  $DC$  in steam. When left at night for subsequent use, an outward pressure was created in all parts of the apparatus.

#### EXPERIMENTAL RESULTS.

The results will be here given as they were for convenience classified during the progress of the work, viz. with dry air in five series, with carbonic acid in two series. The method of reduction of the results is given at page 26, and in my first paper.

##### *Air.*

*First Series.*—This consists of the twenty-one measurements made in 1876 as given at page 49 of the article referred to, and gives as a mean result of the ten measurements of  $\frac{\eta_1}{\eta_2}$  as shown in Table I.

below, the value  $y = \frac{\eta_1}{\eta_2} = 1.234$ , with an average deviation\* of 0.044,

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\* Let  $a_1, a_2, a_3, \dots a_n$ , be a series of measurements of the same quantity, and let  $m$  be their arithmetical mean; then  $a_1 - m = d_1$ ,  $a_2 - m = d_2$ ,  $a_3 - m = d_3$ , &c., will be the deviation of these measurements from their

or about four per cent. A glance at the page referred to will show, however, that of these ten measurements but six were at the temperatures of  $0^\circ$  and  $100^\circ$  respectively. These six as shown in Table II. give the mean

$$y = \frac{\eta_{100}}{\eta_0} = 1.270 \pm a.d. 0.005,$$

and this mean I shall use in comparing this series with the later ones, omitting those results obtained at temperatures between  $0^\circ$  and  $100^\circ$ , because the want of certainty in the temperature measurements would render the labor of the necessary computations fruitless.

TABLE I.

No.	$\frac{\eta_1}{\eta_2}$	$d$ .
2	1.083	-.151
7	1.212	-.022
8	1.206	-.028
9	1.215	-.019
11	1.272	+.038
12	1.267	+.033
13	1.271	+.037
14	1.273	+.039
18	1.277	+.043
21	1.259	+.025
	1.234	0.044

TABLE II.

No.	$\frac{\eta_1}{\eta_2}$	$d$ .
11	1.272	+.002
12	1.267	-.003
13	1.271	+.001
14	1.273	+.003
18	1.277	+.007
21	1.259	-.011
	1.270	0.005

*Second Series.* April, 1878. — In making a study of the best forms of apparatus, a careful trial was given to capillaries in the form of a helix, as these facilitate the maintenance of constant and uniform temperatures of the bath, and render the use of longer and larger tubes possible. The coils were successfully made by winding the tubing, as it was drawn from the tube of the glass-worker, upon a wooden drum. The second series was made with a pair of such coils, and consisted of only eight measurements. The results in the measurements of  $K$  were so wholly discordant, that they were at once rejected.

*Third Series.* — A second pair of smaller coils was mounted in a manner similar to that just described, and with the same general results, showing the coils to be utterly useless; probably, as was to

---

mean, and  $\frac{d_1 + d_2 + d_3 + \dots + d_n}{n}$  will be the average deviation, if, in the summation of the numerator, the values of  $d_1$ ,  $d_2$ , &c. be taken arithmetically, without regard to algebraic sign.

be anticipated, because of changing curvature of the coils owing to expansion or change of position. Several straight capillaries were also studied, varying in size and in the form of tube employed for heating the gas. These experiments covered the whole 126 measurements of this series, and resulted in the selection of the form and size given in the general description of the apparatus at page 2. No systematic study was made, however, of the effects of the proportions of the tube on the law of the transpiration, though the apparatus seems well adapted for that purpose.

*Fourth Series.* October, November, and December, 1878. — The capillaries used in this series were those described in the general account of the apparatus at page 2; viz. straight tubes of about 30 cm. in length and 0.0110 cm. in diameter, and were cut from tube *I* of the apparatus of 1876. The mercury columns were read to 0.1 mm. by a reading telescope from steel millimeter scales placed behind the gauges. Corrections were applied to these scales, but the precision of reading was much less than in the fifth series; the temperature measurements were also somewhat less precise, and the whole series should receive much less weight, owing to the conditions under which it was taken, than the fifth series on air, or the second series on carbonic acid. Table III gives the results obtained.

In the Table the letters heading the columns have the same meaning as elsewhere throughout the paper. The pressures  $p_1$ ,  $p_2$ , &c. are given in millimeters of mercury at 0° C. at Boston. The column headed "Mean  $\frac{\eta_2}{\eta_1}$  or  $K$ ," contains the mean of the group of values of  $\frac{\eta_2}{\eta_1}$ , or of  $K$ , immediately preceding, and a similar statement is true of the column headed "Mean  $t_2$ ."

The results from No. 49 onwards are of much greater precision than those preceding, chiefly from the use of greater pressures, which increased the precision of measurement. Measurements 49 to 99, when combined by the method of least squares, give for constants in the empirical equation

$$\frac{\eta_t}{\eta_0} = \frac{\eta_2}{\eta_1} = 1 + At + Bt^2$$

the values, between the limits  $t = 0^\circ$  and  $t = 100^\circ$ ,

$$A = 0.002821, \text{ and } B = -0.00000149.$$

These values, however, I have regarded as entitled to so much less weight than those of the fifth series for air, that they are given here

TABLE III.—AIR. FOURTH SERIES.

No.	$t_1$	$t_2$	Mean $t_2$	$\frac{\eta_2}{\eta_1}$	Mean $\frac{\eta_2}{\eta_1}$ or $K$	$K$	$P_1$	$P_2$	$P_3$
1	21.4	21.4	°	....	....	1.0571	mm.	mm.	mm.
2	100.0	100.0	....	....	....	1.0471	753.8	639.3	507.8
3	99.94	0.0	....	1.265	1.0521	....	758.5	....	....
4	99.94	0.0	....	1.272	....	....	758.5	610.2	511.8
5	99.94	0.0	....	1.265	....	....	758.5	610.1	510.8
6	99.94	0.0	....	....	....	....	758.5	610.1	510.8
7	99.94	0.0	....	1.266	....	....	758.5	546.0	382.9
8	99.94	0.0	....	1.266	....	....	758.5	546.0	382.9
					1.266				
9	0.0	0.0	....	....	....	1.0542	764.3	645.0	506.5
10	0.0	0.0	....	....	....	1.0574	764.2	645.2	507.6
11	0.0	0.0	....	....	....	1.0585	764.0	645.1	507.8
12	0.0	0.0	....	....	....	1.0517	764.2	606.6	403.1
13	0.0	0.0	....	....	....	1.0520	764.3	569.8	279.3
					1.0548				
21	0.0	16.46	....	1.0308	....	....	763.4	698.3	623.5
22	0.0	16.48	....	1.0380	....	....	763.4	698.5	623.4
23	0.0	16.50	....	1.0355	....	....	763.4	698.2	622.9
			16.48		1.0348				
24	0.0	28.19	....	1.0704	....	....	762.5	699.2	620.5
25	0.0	28.32	....	1.0718	....	....	762.5	699.3	620.6
26	0.0	29.02	....	1.0655	....	....	761.9	698.2	619.1
27	0.0	29.18	....	1.0679	....	....	761.5	697.9	618.7
28	0.0	28.98	....	1.0707	....	....	761.5	698.3	619.5
			28.74		1.0693				
29	0.0	30.49	....	1.0744	....	....	761.5	698.6	619.5
30	0.0	30.41	....	1.0735	....	....	761.5	698.6	619.6
31	0.0	30.30	....	1.0774	....	....	761.4	698.2	618.5
32	0.0	30.12	....	1.0810	....	....	761.4	699.0	620.2
33	0.0	30.06	....	1.0737	....	....	761.4	698.8	620.3
			30.28		1.0760				
34	0.0	37.05	....	1.0945	....	....	761.0	699.6	619.3
35	0.0	37.15	....	1.1016	....	....	760.9	699.9	619.6
36	0.0	37.30	....	1.1035	....	....	760.8	700.2	620.3
37	0.0	37.35	....	1.0982	....	....	760.8	700.2	620.7
			37.21		1.0995				
38	0.0	53.40	....	1.1283	....	....	755.8	698.1	616.3
39	0.0	53.60	....	1.1277	....	....	755.8	698.1	616.3
40	0.0	53.96	....	1.1404	....	....	755.8	697.9	614.7
41	0.0	54.11	....	1.1456	....	....	755.8	697.8	614.0
			53.77		1.1355				
42	0.0	46.28	....	1.1318	....	....	755.3	695.4	611.8
43	0.0	46.68	....	1.1180	....	....	755.0	693.9	609.4
			46.48		1.1249				
44	0.0	56.26	....	1.1432	1.1432	....	754.8	695.4	608.9
45	0.0	68.03	....	1.1740	1.1740	....	754.8	697.4	608.5
46	0.0	66.93	....	1.1725	1.1725	....	754.8	697.2	608.1
47	0.0	67.88	....	1.1752	....	....	755.0	697.0	607.0
48	0.0	67.83	....	1.1748	....	....	755.0	696.8	606.5
			67.86		1.1750				
49	0.0	0.0	....	....	....	....	759.2	557.0	238.0
50	0.0	0.0	....	....	....	....	759.2	557.0	238.0
51	0.0	0.0	....	....	....	1.0517	759.3	556.7	237.6
52	0.0	0.0	....	....	....	1.0520	759.3	556.5	236.7
53	0.0	0.0	....	....	....	1.0517	759.9	556.1	232.9
54	0.0	0.0	....	....	....	1.0522	759.9	556.1	232.8
					1.0519				

Tube I. remounted

TABLE III. — Continued.

No.	$t_1$ .	$t_2$ .	Mean $t_2$ .	$\eta_2$ $\eta_1$	Mean $\eta_2$ or $K$ $\eta_1$	$K$ .	$P_1$ .	$P_2$ .	$P_3$ .
							mm.	mm.	mm.
55	0.0	42.80	.....	1.1202	....	....	761.4	586.7	232.9
56	0.0	42.84	.....	1.1200	....	....	761.5	586.6	232.0
57	0.0	42.84	.....	1.1187	....	....	761.6	586.7	232.9
58	0.0	42.95	.....	1.1216	....	....	762.0	587.1	231.7
59	0.0	42.95	.....	1.1216	....	....	762.0	587.1	231.7
			42.88		1.1204				
60	0.0	0.0	.....	.....	.....	1.0526	760.4	556.6	234.1
61	0.0	0.0	.....	.....	.....	1.0506	760.3	556.6	233.4
62	0.0	0.0	.....	.....	.....	1.0535	760.1	555.1	228.5
63	0.0	0.0	.....	.....	.....	1.0524	760.1	555.2	228.4
64	0.0	0.0	.....	.....	.....	1.0498	759.9	555.6	229.1
65	0.0	0.0	.....	.....	.....	1.0504	759.9	555.6	229.4
66	0.0	0.0	.....	.....	.....	1.0507	759.9	555.5	229.1
					1.0514				
67	0.0	72.55	72.55	1.1913	1.1913	....	760.8	602.3	229.6
68	0.0	12.57	....	1.0372	....	....	754.3	559.5	221.5
69	0.0	12.67	....	1.0366	....	....	754.3	559.3	220.6
70	0.0	12.77	....	1.0371	....	....	754.3	559.4	220.6
71	0.0	12.92	....	1.0368	....	....	754.2	559.3	220.3
72	0.0	12.92	....	1.0365	....	....	754.1	559.2	220.3
73	0.0	12.92	....	1.0365	....	....	754.1	559.2	220.3
			12.80		1.0368				
74	0.0	21.50	....	1.0583	....	....	753.9	565.0	221.1
75	0.0	21.15	....	1.0589	....	....	753.8	565.2	222.9
76	0.0	20.85	....	1.0599	....	....	753.7	564.3	218.5
77	0.0	20.65	....	1.0602	....	....	753.7	564.4	219.3
78	0.0	20.40	....	1.0582	....	....	753.7	563.4	215.6
			20.91		1.0591				
79	0.0	20.15	....	1.0557	....	....	753.7	563.0	215.4
80	0.0	19.80	....	1.0561	....	....	753.7	562.9	215.4
81	0.0	19.65	....	1.0541	....	....	753.7	562.6	215.3
			19.87		1.0553				
82	0.0	40.01	....	1.1100	....	....	753.7	575.9	214.0
83	0.0	39.91	....	1.1116	....	....	753.8	576.1	214.0
84	0.0	39.88	....	1.1081	....	....	753.8	576.0	214.0
85	0.0	39.93	....	1.1111	....	....	754.3	576.5	214.5
			39.93		1.1102				
86	0.0	62.64	....	1.1690	....	....	754.8	590.1	214.2
87	0.0	62.59	....	1.1699	....	....	754.8	590.1	213.8
88	0.0	62.39	....	1.1706	....	....	754.8	590.1	213.8
89	0.0	62.34	....	1.1687	....	....	754.9	590.0	213.9
90	0.0	62.34	....	1.1684	....	....	754.9	590.0	214.1
			62.46		1.1693				
91	0.0	79.92	....	1.2174	....	....	755.4	600.2	214.3
92	0.0	80.02	....	1.2159	....	....	755.4	600.1	214.3
93	0.0	79.62	....	1.2170	....	....	755.4	600.1	214.3
94	0.0	79.32	....	1.2149	....	....	755.5	599.9	214.4
95	0.0	79.32	....	1.2143	....	....	755.5	599.8	214.1
96	0.0	79.27	....	1.2134	....	....	755.6	599.8	214.2
			79.58		1.2155				
97	0.0	99.66	....	1.2655	....	....	751.2	606.0	210.3
98	0.0	99.66	....	1.2657	....	....	751.2	605.2	204.0
99	0.0	99.66	....	1.2685	....	....	751.2	605.2	502.9
			99.66		1.2666				

merely as a satisfactory and important check upon the further results of that series. The equation deduced from this latter series, I regard as best representing my measurements on dry air. It will be noticed, on comparing the two series, that the greatest deviation of the two series is at  $100^{\circ}$ , where it amounts to less than 0.4 per cent.

Measurements 1 and 2 were taken during preliminary trials of the apparatus. In 3 to 8 the first capillary was in boiling water, the second in ice, this reversal of the usual sequence of temperatures being made in order to test the apparatus. The mean of these five measurements (the sixth having been rejected when made, as having been taken before the static condition of the process was reached) gives

$$y = \frac{\eta_{100}}{\eta_0} = 1.267 \pm a.d. 0.002.$$

The above equation gives for  $t = 99^{\circ}.94$

$$\frac{\eta_t}{\eta_0} = 1.2666,$$

and the direct observation made, as were all those from which the equation is derived, with the first capillary at  $0^{\circ}$ , gives as the mean at  $99^{\circ}.66$

$$\frac{\eta_t}{\eta_0} = 1.2666.$$

The close agreement of these numbers seems to indicate a freedom from constant error of any considerable magnitude in the value of  $K$  and in the expansion correction to this value.

*Fifth Series.* April, 1880.— This series was taken with the apparatus as described at page 2, immediately after the completion of the second series with carbonic acid. The measurements were made under as favorable conditions as any of this paper, and are of greater weight than all of the others upon air. The full data for the computation of these results are given in Table IV. in such form that a recomputation, in so far as relates to those portions subject to possible modification of such amount as to materially change the result, may at any time be made. The value of  $K$  used was the same as that used for the second series of carbonic acid.

These measurements may be divided according to temperatures into six groups, and are very concordant except that the sixth group shows a deviation of about 0.6 per cent from the value which the other five groups would indicate at that temperature. There appears

TABLE IV.—AIR. FIFTH SERIES.

No.	$p_1-p_2$	$p_1+p_2$	$p_3-p_4$	$p_3+p_4$	$\alpha$	$t_2$	$\frac{\eta_2}{\eta_1}$	Computed $\frac{\eta_2}{\eta_1}$	d.
1	92.31	1418.23	113.29	1212.63	.0036693	13.70	1.0374		
2	92.26	1417.90	113.37	1212.27	.....	13.93	1.0378		
3	92.15	1417.71	113.35	1212.21	.....	14.21	1.0378		
					Means =	13.947	1.0377	1.0383	-.0006
4	83.93	1423.93	122.09	1217.91	.0036694	42.60	1.1180		
5	83.86	1423.50	122.13	1217.51	.....	43.04	1.1178		
6	83.81	1423.35	122.27	1217.27	.....	43.30	1.1187		
7	83.98	1422.78	122.41	1216.39	.....	43.17	1.1178		
8	83.98	1422.44	122.25	1216.21	.....	42.76	1.1179		
					Means =	42.974	1.1180	1.1176	+.0004
9									
10	77.39	1425.25	128.88	1218.98	.0036694	67.74	1.1861		
11	77.34	1425.16	128.76	1219.06	.....	67.74	1.1859		
12	77.34	1425.08	128.83	1218.91	.....	67.94	1.1831		
					Means =	67.81	1.1850	1.1850	.0000
13	72.44	1429.96	133.48	1224.04	.0036695	88.67	1.2381		
14	72.29	1430.11	133.59	1224.23	.....	88.64	1.2419		
15	72.20	1430.14	133.49	1224.45	.....	88.85	1.2419		
16	72.20	1429.96	133.59	1224.17	.....	88.92	1.2424		
					Means =	88.77	1.2411	1.2415	-.0004
17	70.20	1441.48	136.41	1234.87	.0036696	99.69	1.2684		
18	70.28	1441.22	136.35	1234.59	.....	99.02	1.2686		
19	70.23	1440.51	136.58	1233.70	.....	98.93	1.2716		
20	70.05	1440.43	136.11	1234.27	.....	99.41	1.2695		
21	70.05	1440.19	136.14	1234.00	.....	99.03	1.2710		
22	70.10	1440.10	136.16	1233.84	.....	99.18	1.2695		
					Means =	99.21	1.2698	1.2696	+.0002
23	64.94	1446.20	141.17	1240.09	.0036697	124.61	1.3321		
24	64.86	1446.46	141.21	1240.39	.....	124.36	1.3350		
25	65.12	1446.42	140.95	1240.35	.....	124.17	1.3279		
26	64.98	1446.72	141.02	1240.70	.....	124.22	1.3314		
27	65.12	1446.94	140.96	1240.86	.....	124.69	1.3264		
					Means =	124.41	1.3306	1.3368	-.0062

to be in this group some considerable constant error, due probably to a mistake in the reading of the thermometer which was a different one, from that used in the preceding groups. The deviation is so large that I have thought it best to reject the sixth group wholly in the computation of the empirical equation for this series on air. I fully recognize that this rejection may be considered somewhat arbitrary, and also that the retention of the sixth group would make the accordance between the fourth and fifth series greater than now; but I am so fully satisfied that there is some mistake in the rejected group

that I unhesitatingly lay it aside. I thus obtain by the method of least squares for measurements 1 to 22 on dry air, 5th series,

$$\frac{\eta_t}{\eta_0} = 1 + 0.002751 t - 0.00000034 t^2,$$

between the temperature limits of  $0^\circ$  and  $100^\circ\text{C}$ . The last column of the table, headed  $d$ , gives the deviations of the observed means from the values of  $\frac{\eta_t}{\eta_0}$ , computed for the same temperatures  $t_2$  by the preceding equation and given in the ninth column. The average deviation of the means from the equation is thus only 0.0003, or about 0.03 per cent, for the first five means, the deviation of the sixth mean being ten times the next greatest deviation. The average deviation of the individual observations from their respective means, disregarding the correction corresponding to the slight differences of the observed temperatures from the mean, is 0.0012 or about 0.1 per cent.

#### Carbonic Acid. $\text{CO}_2$ .

*First Series.*— 21 measurements were made in January, 1879, after the close of the fourth series on air, and with the same apparatus, with the addition of the necessary apparatus for holding the gas. The precision of the results was less than in the fourth series for air, chiefly because of the somewhat greater complication of the apparatus for the supply of the gas. The results are of little value, but are given as a check on the second series. The pressures were about the same as in Nos. 49 to 98 of the fourth series on air. The temperature  $t_1$  of the first capillary was always  $0^\circ\text{C}$ . The following Table V. gives the mean results. The coefficient of expansion used was 0.003699, a value taken from Regnault's work by interpolation for the actual pressure  $p_2$ , under which the expansion occurs.

The column headed  $n$  gives the number of measurements going to make up the corresponding means.

TABLE V. —  $\text{CO}_2$ . FIRST SERIES.

$n$ .	$t_2$	$\frac{\eta_2}{\eta_1}$	Computed $\frac{\eta_2}{\eta_1}$
8	29.61	1.103	1.108
5	48.60	1.178	1.175
8	100.09	1.324	1.351

*Second Series.*—120 measurements were made from January to April, 1880, with the complete apparatus as described at pages 2 and 9. The thermometers used were Casella 32378, Baudin 7335 up to  $180^{\circ}$ , and Baudin 7789 above  $200^{\circ}$ . The first 20 measurements were preliminary, being made with various tubes and forms of apparatus before satisfactory forms were obtained. The remainder are given in the following table. In all cases  $t_1 = 0^{\circ}$ .

TABLE VI.—CO<sub>2</sub>. SECOND SERIES.

No.	$p_1$ .	$p_2$ .	$p_3$ .	$K$ .	Mean $K$ .
1	784.08	720.53	653.77	1.0422	1.0440
2	786.69	720.17	653.99	1.0918	
3	787.48	721.58	654.10*	1.0737	
4	785.44	722.30	654.54	1.0204	
5	790.61	724.59	654.84	1.0397	
6	758.59	700.78	640.07	1.0364	
7	758.17	700.30	639.71	1.0638	
8	757.60	699.82	639.23	1.0380	
9	757.15	699.27	638.57	1.0381	
10	773.74	707.56	637.41	1.0390	
11	774.14	707.50	636.92	1.0169	
12	780.55	718.34	652.49	1.0330	
13	780.74	718.12	652.18	1.0387	
14	748.64	699.58	649.47	1.0510	1.0375
15	748.45	699.99	649.37	1.0276	
16	748.27	699.72	649.27	1.0330	
17	748.52	699.55	648.81	1.0365	
18	748.37	699.34	648.75	1.0408	
19	748.19	699.33	648.68	1.0359	
20	771.58	614.35	409.82	1.0402	1.0395
21	771.62	614.36	409.70	1.0376	
22	771.66	614.35	409.57	1.0390	
23	771.67	614.28	409.22	1.0394	
24	772.11	614.50	409.16	1.0397	
25	772.38	614.57	408.98	1.0401	
26	770.73	611.24	400.91	1.0353	1.0380
27	770.55	610.67	400.83	1.0404	
28	770.37	610.55	400.81	1.0404	
29	771.92	701.15	625.09	1.0335	
30	771.71	700.74	624.08	1.0366	
31	771.50	700.54	624.90	1.0419	
32	767.36	705.39	640.08	1.0386	
33	767.46	705.46	640.22	1.0394	
34	766.90	705.13	639.89	1.0362	
35	766.80	705.01	639.71	1.0357	
36	767.34	712.33	655.13	1.0406	
37	767.29	712.39	655.18	1.0383	
38	766.95	712.12	654.91	1.0370	

TABLE VI.—CO<sub>2</sub>. SECOND SERIES.—*Continued.*

No.	$P_1$ .	$P_2$ .	$P_3$ .	100 a.	$t_2$ .	$\frac{\eta_2}{\eta_1}$ .	Mean $t_2$ .	Mean $\frac{\eta_2}{\eta_1}$ .	Computed $\frac{\eta_2}{\eta_1}$ .
39	746.72	693.79	630.67	0.37047	17.62	1.0688	18.10	1.0679	1.0666
40	746.53	693.62	630.49		17.87	1.0684			
41	746.18	693.31	630.10		18.09	1.0696			
42	745.93	692.94	629.77		18.29	1.0658			
43	745.64	692.71	629.47		18.62	1.0669			
44	745.41	696.50	628.79	0.37053	41.15	1.1468	40.98	1.1458	1.1485
45	745.64	696.68	629.03		41.28	1.1472			
46	745.97	697.01	629.24		40.86	1.1481			
47	746.41	697.32	629.70		40.86	1.1426			
48	746.73	697.75	630.22		40.87	1.1438			
49	747.45	698.54	630.98		40.87	1.1461			
50	769.40	723.90	653.79	0.37071	59.02	1.2125	59.14	1.2126	1.2119
51	769.56	724.17	653.75		59.30	1.2197			
52	769.49	724.18	654.04		59.54	1.2164			
53	769.47	724.20	654.31		59.50	1.2163			
54	769.25	723.90	654.43		58.93	1.2064			
55	769.23	723.89	654.25		58.72	1.2102			
56	769.26	724.01	654.68		58.96	1.2068			
57	774.14	732.22	659.65	0.37077	79.56	1.2847	79.65	1.2848	1.2820
58	774.07	732.31	659.96		79.58	1.2860			
59	773.93	732.35	660.33		79.72	1.2857			
60	773.66	732.17	660.48		79.73	1.2829			
61	773.71	735.84	662.96	0.37081	99.67	1.3550	100.17	1.3506	1.3508
62	773.62	735.83	663.22		100.17	1.3514			
63	773.50	735.77	663.52		100.24	1.3468			
64	773.78	736.13	663.86		100.60	1.3490			
65	780.77	745.42	670.80	0.37087	119.11	1.4147	119.30	1.4148	1.4139
66	780.70	745.31	670.68		119.20	1.4129			
67	780.32	745.04	670.69		119.27	1.4120			
68	779.81	744.65	670.56		119.37	1.4119			
69	779.58	744.58	670.24		119.55	1.4223			
70	770.66	738.34	663.10	0.37083	141.53	1.4774	141.893	1.4843	1.4873
71	770.52	738.18	662.91		141.89	1.4757			
72	770.55	738.38	663.11		141.90	1.4836			
73	770.43	738.52	663.31		141.87	1.4948			
74	770.18	738.28	663.31		141.92	1.4919			
75	769.77	737.82	663.10		142.25	1.4824			
76	766.48	734.44	652.66	0.37078	158.40	1.5402	158.283	1.5371	1.5400
77	766.22	734.26	652.58		158.83	1.5498			
78	766.06	734.26	653.19		159.44	1.5446			
79	765.38	733.54	652.85		159.05	1.5415			
80	763.89	732.12	652.69		157.87	1.5218			
81	763.60	731.91	652.61		157.56	1.5244			
82	763.28	731.73	652.46		157.62	1.5341			
83	763.05	731.63	652.45		157.50	1.5310			

TABLE VI.—CO<sub>2</sub>. SECOND SERIES.—*Continued.*

No.	$p_1$ .	$p_2$ .	$p_3$ .	100 a.	$t_2$ .	$\frac{\eta_2}{\eta_1}$ .	Mean $t_2$ .	Mean $\frac{\eta_2}{\eta_1}$ .	Computed $\frac{\eta_2}{\eta_1}$ .
84	773.83	745.39	666.15	0.37088	181.49	1.6141	181.32	1.6188	1.6185
85	773.96	745.70	666.23		180.99	1.6309			
86	773.97	745.67	666.23		180.96	1.6280			
87	774.14	745.64	666.21		181.70	1.6136			
88	774.01	745.49	666.38		181.45	1.6072			
89	774.41	747.71	660.30	0.37090	223.9	1.7284	224.0	1.7474	1.7488
90	774.32	747.94	661.30		225.0	1.7312			
91	773.99	747.87	660.78		223.4	1.7631			
92	774.33	748.38	661.66		223.7	1.7669			
93	771.47	722.92	666.03	0.37071	16.20	1.0668	17.07	1.0630	1.0628
94	770.89	722.21	665.19		16.62	1.0646			
95	769.33	677.80	561.76	0.37036	17.18	1.0602			
96	769.14	677.75	561.63		17.30	1.0621			
97	768.79	677.40	561.21		17.47	1.0620			
98	768.73	677.88	561.12		17.62	1.0625			

Measurements 39 to 98 furnish data for computing the constants in an empirical equation for carbonic acid, and the equation thus deduced is

$$\frac{\eta_t}{\eta_0} = 1 + 0.003725t - 0.00000264t^2 + 0.00000000417t^3,$$

between the limits of 0° and 224° C.

The term containing  $t_3$  is necessary on account of the rapid curvature of the line representing the observations. The last column of Table VI. shows the values of  $\frac{\eta_2}{\eta_1} = \frac{\eta_t}{\eta_0}$  deduced from this equation for the temperature means of the second column, showing as close an agreement with the observed means of  $\frac{\eta_2}{\eta_1}$  as could be expected except at 100°, where the deviation amounts to about two per cent. The first series is however of much less weight than the second series. The last column of Table VI. shows the values of  $\frac{\eta_2}{\eta_1}$  computed to correspond with the means of the preceding column. The average deviation of the observed means from those computed from the above equation is thus 0.0020 or about 0.15 per cent. The average deviation of the individual results from their corresponding means, taken as in the fifth series for air, is 0.0052, or about 0.4 per cent.

*Effect of Pressure.*

In Series IV. for air, the total driving pressure used,  $p_1 - p_3$ , was varied within considerable ranges, to test whether the value obtained of  $\eta_2 : \eta_1$ , or of  $K$ , was thereby affected except through errors of observation. In 3, 4, and 5,  $p_1 - p_3 = 248$  mm., and  $\eta_2 : \eta_1 = 1.267$ ; in 7 and 8, under the same conditions otherwise,  $p_1 - p_3 = 376$  mm., and  $\eta_2 : \eta_1 = 1.266$ , showing no effect due to increase of the pressure by one half. Measurements 9 to 13, made with  $p_1 - p_3$  ranging from 258 to 485 mm., give values of  $K$  with an average deviation of about 0.2 per cent. Measurements 21 to 48 give values of  $\eta_2 : \eta_1$  about one per cent lower than those obtained in the remainder of the series, made with greater values of  $p_1 - p_3$ , but the precision of these measurements is much less than of the later ones. The value of  $K$  found from 50 to 54 and 60 to 66, with  $p_1 - p_3 = 530$  mm. about, is within 0.5 per cent of that found in 9 to 12, under  $p_1 - p_3 = 258$  mm., and agrees precisely with 12, under  $p_1 - p_3 = 361$  mm. And, finally, the mean of 97 and 98 differs from 99 by less than 0.25 per cent, though the pressures  $p_1 - p_3$  are respectively 540 and 250 mm.

In the second series for carbonic acid, the effect of pressure was somewhat tested in measurements 26 to 38, where  $p_1 - p_3$  varied from 370 to 111 mm. without producing any traceable effect in  $K$ . This is the best test made, owing to the greater precision of the measurements. Also in measurements 93 to 98 of the same series the pressure was changed from 105 to 207 without materially affecting the results.

In the first series for air, the average value of  $p_1 - p_3$  was about 740 mm., and the mean value of  $\eta_2 : \eta_1$  at  $t_2 = 100^\circ$  is 1.270, while that of the fourth series, under  $p_1 - p_3 =$  from 248 to 540, is about 1.267, and that of the fifth series, under  $p_1 - p_3 = 225$  mm., is 1.272, thus showing no effect traceable to the difference of the driving pressures used.

*Deduction from Results.*

The results of my measurements seem to show conclusively, that the variation of the viscosity with the temperature of the gas, in the case at least of dry carbonic acid and of dry air freed from carbonic acid, which may be taken as typical gases, is not proportionate either to the square root or to any numerical power of the absolute temperature reckoned from  $-273^\circ \text{C}$ . They point thus to the inference that all hypotheses yet advanced to account for the variation of the viscosity

of gases, and hence also for the viscosity itself, are incomplete for this phenomenon, in the same general way as are the analogous hypotheses regarding the compressibility of gases and other phenomena. The hypothetical deductions fail to accord completely with the results of quantitative measurements.

#### DISCUSSION OF RESULTS OF ALL RESEARCHES ON AIR AND CO<sub>2</sub>.

The experimental results which I have given in the foregoing tables, and the deduced equations, show that, unless some considerable and regular source of error affects them, the viscosity of both dry air (freed from CO<sub>2</sub>) and carbonic acid increases with the rise of temperature according to a rate which varies with the temperature and is smaller as the temperature is higher. The ratio  $\eta_t : \eta_0$  is therefore not proportional to the first power (Maxwell) of the absolute temperature; it is not expressible by a linear equation of the first degree, e. g.  $\eta_t = \eta_0 (1 + b t)$ , where  $t$  = temperature C. and  $b$  = a constant; nor is it given by the equation  $\eta_t = \eta_0 (1 + a t)^n$ , or its equivalent  $\eta_t \div \eta_0 = c \tau^n$ , where  $\tau$  = absolute temperature. The last three equations are the only ones thus far used by observers in discussing their results, although the work of E. Wiedemann and A. von Obermayer shows a decided departure from these expressions. The insufficiency of the latter equations may be shown by discussing the observational data by the logarithmic method which I used in my former paper. Nor could the equation  $\eta_t = \eta_0 (1 + a t)^n$  be more than an empirical equation at best, unless possibly when  $a$  were expressed as a function of  $t$  and the pressure, a condition which I have not thought worth consideration at present. For the expression of my own results, I have employed merely the empirical equation with increasing powers of  $t$ , as I have found no theoretical hypothesis which led to results corresponding to the observed relation of  $\eta$  and  $t$ .

The deviation of both air and carbonic acid from the equation  $\eta_t = \eta_0 (1 + b t)$  is so small, and the difficulties of precise measurement so considerable, that these deviations may often be masked by accidental errors of measurement, and by "constant errors," arising from imperfect drying or purification of the gas, from differences between the thermometer indications and the actual temperature of the gas, from faulty proportioning of apparatus, and from other sources. This discussion of my own method in these regards I give at page 25; that of others, I cannot advantageously attempt. But I

will proceed to a review of the results obtained by all others who have worked in this field; and shall show that for air and carbonic acid no results are found giving a value of  $b$  (rate of change of  $\eta_t : \eta_0$  with rise of temperature) increasing with the temperature; that some results can give only a constant value to  $b$ , owing either to the want of sufficient precision, or to the insufficient number of temperature intervals employed; that some results show a marked diminution, as do my own, of  $b$ ; and that many of these last, when carefully discussed, afford material for getting at a numerical measure of the change in  $b$  which is in substantial accordance with my own results. These facts indicate, either that all measurements show conclusively that  $b$  does diminish with rise of temperature, or that the method of transpiration through capillary tubes upon which these demonstrations rest (for the measurements with oscillating plates are of insufficient precision for determination of this change) is faulty in either its experimental application or its mathematical theory. In the consideration of this last proposition the statements which I have made at page 25 should be reviewed.

In the discussion of the results of former observers, I have adopted the graphical method as best adapted to the purpose; but as the point to be considered is one in which changes in the fourth and sometimes the fifth place of significant figures must be exhibited, a special device must be resorted to. I have therefore assumed for carbonic acid an equation  $\eta_t = \eta_0 \left(1 + \frac{t}{300}\right)$ , and for air  $\eta_t = \eta_0 \left(1 + \frac{t}{400}\right)$ , as convenient equations to which to refer the results on these gases respectively. I have computed for two or many temperatures (usually those of observation) values of  $\eta_t : \eta_0$  from these equations, and subtracting these from the experimental data for the same temperature (or from ratios  $\eta_t : \eta_0$  deduced by myself from the data), I have obtained differences or residuals which I have used as ordinates in the lines shown in the plots on Plates I. and II. These lines or "residual curves"\* easily show the fourth place of decimals in the ratio  $\eta_t : \eta_0$ , and develop as a curvature the change of the rate  $b$ . As the residual curves are plotted, convexity upwards shows a diminution of  $b$  with rise of  $t$ , concavity upwards would show an increase of  $b$ , and no curvature of course indicates a constant value of  $b$ . Above and below the  $50^\circ$ ,  $100^\circ$ , and  $200^\circ$  points of my own results will be seen a vertical row of points marked 1 %, 2 %, -1 %, etc., which indicate dif-

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\* See Pickering, *Physical Manipulation*, i. 12; *Jour. Franklin Inst.*, lxi. 272.

ferences in  $\eta_t : \eta_0$  of 1, 2, etc. per cent from my results, and afford a convenient means of comparing the relative concordance between the results of various observers. It should be borne in mind, however, that some of the lines are plotted from means, some from single observations, and others from equations deduced either by the observers or by myself. The individual points, therefore, must not be used without qualification as a measure of the precision of the results obtained by any single observer.

### *Carbonic Acid, CO<sub>2</sub>.*

The curve *OA* on Plate I. is from the equation deduced at page 17 for my own results. There can be no question as to the decided curvature shown being far beyond the limits of variable experimental error. My computations have also shown that the third power of the temperature in the linear equation was necessary. The experimental means are marked along the curve.

The curve *DOB* is from an equation of the same form

$$\eta_t = \eta_0 (1 + At + Bt^2),$$

in which *A* and *B* are computed from the results of A. von Obermayer\* with capillary "I." The term *Ct<sup>3</sup>* was omitted because of the smaller number of points and their somewhat less precision. That the line represents approximately the data will be seen from noting the distribution about it of the observed points. The curvature is here also undoubted, although Obermayer merely remarks that "it follows from these experiments with some probability that the increase in coefficient of friction with rising temperature is less at higher than at lower temperatures." A comparison of this curve with mine shows that Obermayer's results and my own are in substantial agreement as to the rate of change in *b*, the curvature of the two lines being very nearly the same. Indeed, if my results be thrown into the same equation, using only the first and second powers of *t*, the value of *B* becomes 0.00000136, while that from Obermayer's data is *B* = 0.00000137. The value of *A* from my results is, however, considerably larger than from Obermayer's, so that his value of  $\eta_t : \eta_0$  at 100° is about 0.7 per cent below mine, and at 200° about 1 per cent below. The line *OC* is from the equation

$$\eta_t = \eta_0 (1 + 0.003582t - 0.00000105t^2),$$

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\* A. VON OBERMAYER, Wien. Ber., lxxiii. 468 (1876).

deduced by me from Obermayer's experiments at the three indicated temperatures with the capillary "D." This is in still closer agreement with mine in numerical values of  $\eta_t : \eta_0$ , but has slightly less curvature ( $B = 0.00000105$ ). The value for  $A$  in my results is 0.003637, with the same terms in the equation. When methods as different in detail as those of Obermayer and myself are in so close agreement as these appear to be when thus discussed, the chances of large constant errors other than those inherent in the use of transpiration methods seem to be much reduced.

On the line  $JH$  are three points showing the results obtained by Eilhard Wiedemann. The line is drawn from the equation

$$\eta_t = \eta_0 (1 + 0.003727 t - 0.00000320 t^2),$$

which I have deduced from these three points. The curvature is much greater than for either of the other lines, the value of  $B$  being more than twice as great as in the lines  $OA$  and  $OB$ , and three times as great as in  $OC$ . A reference to my discussion of the results for air will show that Wiedemann's results there exhibit similar relative characteristics. Up to  $100^\circ$  for  $\text{CO}_2$  the results differ numerically by less than 0.7 per cent from those of Obermayer and myself, but at  $200^\circ$  the difference is nearly 3 per cent.

The results by Puluj, as shown by the line  $OF$ , obtained by oscillating plates, are smaller than all others, a difference which characterizes his results for air. The range of temperature used is too limited to render the results available in the present consideration.

*Conclusion.*—In the absence of any really satisfactory means of assigning proper weights to the results of Obermayer, Wiedemann, and myself, it seems best to allow the results to stand in the form above given, without an attempt to deduce a mean.

#### *Air.*

In Plate II. are shown the residual curves for all available observations on air. The line  $IJ$ , representing Maxwell's results, doubtless owes its steepness to some large constant error, for which several explanations have been offered. The lines for O. E. Meyer's results from capillary transpiration are

$$\begin{array}{lll} AB \text{ from Eqn. } \eta = 0.000171 (1 + 0.0024 t), & \text{Range } 20^\circ \text{ to } 99^\circ; \\ CD \text{ " " } \eta = 0.000170 (1 + 0.0028 t), & \text{" " } 21^\circ \text{ to } 100^\circ; \\ EF \text{ " " } \eta = 0.000174 (1 + 0.0030 t), & \text{" " } 21^\circ \text{ to } 100^\circ; \end{array}$$

and from oscillating plates the line is  $GH$  from the mean of the equations,

$$\eta = 0.000186 (1 + 0.0030 t),$$

and  $\eta = 0.000189 (1 + 0.0025 t),$  Range  $19^\circ$  to  $82^\circ$ ,

given for different methods of computing one series of data. It is perhaps worthy of remark, that the mean of Meyer's results at  $100^\circ$  agrees with the results of my fifth series within 0.2 per cent. Meyer's observations were made chiefly at two temperatures, and thus, as well as on account of the magnitude of the errors of observation, are incapable of indicating the small deviation of  $\eta_t : \eta_0$  from the equation of the first power of  $t$ .

The observations of Puluj are shown by the lines  $KL$ ,  $MN$ ,  $OP$ ,  $QR$ , and  $ST$ , of which all but  $ST$  are from transpiration experiments, this being by oscillating plates. From the data which I have used in plotting the lines Puluj deduces the first power equations:—

$KL$ , $\eta = 0.000179 (1 + 0.0024 t),$	Range $13^\circ.0$ to $27^\circ.0$ .
$MN$ , $\eta = 0.000179 (1 + 0.0023 t),$	" $13^\circ.6$ to $76^\circ.7$ .
$OP$ , $\eta = 0.000181 (1 + 0.0022 t),$	" $1^\circ.1$ to $77^\circ.4$ .
$QR$ , $\eta = 0.000180 (1 + 0.0021 t),$	" $1^\circ.5$ to $92^\circ.7$ .
$ST$ , $\eta = \text{constant } (0.03855 + 0.00010213 t)$	" $-3^\circ.0$ to $25^\circ.0$ .

From the plots on Plate II., and from others which I have made, it appears to me that the data shown in  $KL$  cannot be represented by a straight line, nor are they to be relied upon for giving the rate of change of  $\eta_t : \eta_0$  at all, the curvature of the line  $KL$  which approximately represents the data being undoubtedly the result of uncorrected constant error. The points of the line  $MN$  show an upward convexity of slight amount; those of the line  $OP$  are so irregularly distributed as to conceal any slight systematic deviation from the straight line. The points of  $QR$  are also very irregularly distributed, but are unquestionably more nearly represented by the line  $QR$ , which I have drawn approximately through them, than by the straight line  $SR_1$ , which corresponds to the equation given by Puluj, or by any other straight line. The line  $QR$  should certainly be convex upwards.

The numerous experiments of Obermayer give almost unquestionable evidence that even for air the coefficient of viscosity increases at a less rapid rate at higher than at lower temperatures. The line  $aSbc$  represents the mean of results by capillaries "11," "26," and

"D." (I was obliged to omit "I" from consideration, owing to an apparent error. Wien. Ber., lxxiii. 440.) The separate results are fairly accordant. This line agrees quite closely with my fifth series, *SY*. The results obtained with a brass capillary are indicated by the line *de*, which is a continuation also of *Sb*, since the brass capillary agreed substantially with the others at *b*. The curvature of this line, as well as of *aSbc*, is decidedly convex upward, much more so than *SY*. Obermayer's further series with capillary "D" is of much value. It is represented in the line *gh*, and the three marked points indicate the points yielded by the experiments. This line is also decidedly convex upward, and its curvature seems to be beyond the range of variable errors of measurement. I have connected the individual points with each other by a broken line, because, owing to the small number of points, almost any form of curve could be drawn through them, and to select any one equation would be wholly arbitrary. This remark applies also to the line *UV*, representing Wiedemann's results. This line is still more convex upward than either of the preceding. The line *WX*, representing Warburg's results with oscillating plates, is in substantial accord with the results by Obermayer, Wiedemann, and myself, as well as with the mean of Meyer's results; but as it is derived from observations including but one temperature interval, it cannot serve to determine any beyond the first power variation in the coefficient.

To show the relation of the several lines to one from an equation of the exponential form which has been so generally adopted, I have drawn the line *Z* from the equation

$$\frac{\eta_t}{\eta_0} = (1 + 0.003670)^{0.76}.$$

The fifth series of my own results is shown in the line *SY*, the experimental means being denoted by crosses. The deviation of *SY* from a straight line is quite slight, and I am confident that this is a close approximation to the true result, and that the greater curvature of the lines from my own earlier results and those of other observers is due in part to impurities in the air, either in the form of carbonic acid or of vapor of water. I regard those of my measurements on air which precede the fifth series merely as checks upon the accuracy of the process, and as possessing small weight as compared with that series, for reasons assigned in the following Critique of the Method. The same is true of all but the last series with carbonic acid.

## CRITIQUE OF THE METHOD.

Since the variation to be studied in the present investigation is one of quite small amount, and is determined as the result of a somewhat complex measurement, any systematic error of even quite small magnitude might mask the quantity sought. It is essential, therefore, to show how far such errors of sensible magnitude have been avoided or eliminated. In the following pages I have given a somewhat detailed discussion of the possible sources and magnitudes of error in my measurements, and of the accuracy attained in the various component measurements.

The advantages of the method arise from its simplicity and directness. The only measurements of precision required are of the temperature of the second capillary, and of the lengths of several mercury columns. No measurements of volume are involved. The two capillaries through which identically the same masses of gas are successively transpired are as nearly as possible alike, and under the same conditions except as to temperature. The gas is transpired through each under nearly the same pressure difference, and at a pressure not far from one atmosphere. The flow of the gas is perfectly uniform, except for slight accidental fluctuations, throughout the whole of a measurement or set of measurements, tending thus to the elimination of a class of errors possible in such methods as that of oscillating plates, or of transpiration when the driving pressure falls from a given initial to a less final amount. The disturbing effect of eddies, or other special action, at the entrance to or exit from the tube, would be in part eliminated in this method, since the measurements give the ratios of the resistance in two tubes under constant and nearly identical conditions. No complete discussion of these effects has been yet given, and their experimental elimination certainly seems more easy than their mathematical treatment. It seems quite possible that they are still sensible sources of deviation from the assumed law of transpiration, but as the magnitude of the disturbance is small, and cannot be widely different in the two tubes used in this apparatus, and since the determination of the constants of the tubes dependent on their diameters, lengths, &c. are experimentally made by the same process and under conditions identical with the subsequent work, the resulting error must be small. It should be noted, also, that the debated question as to the slip of the gas over the inner surface of the glass tube has an influence in my results only to the extent by which this slip is affected by the temperature.

The freedom of the method from constant error is indicated by the close accordance of the results on dry air as obtained by the first, fourth,

and fifth series. The first series was made with an apparatus totally different from that afterwards used in all details of disposition of parts and of instruments used, except that the tube *I* of that series was the same that was afterward cut into three pieces, of which two nearly equal ones served as the capillaries in the fourth and fifth series. Observations with other tubes in the preliminary measurements, however, checked satisfactorily with these. The instruments and arrangements for measuring the pressures in the fourth series were wholly different from those used in the fifth series. The results at 100° for the three series are given in the following Table VII., in which the last two values are taken from the equation deduced for the respective series.

TABLE VII.

Series.	$\frac{\eta_{100}}{\eta_0}$ .	<i>d.</i>
I.	1.270	—0.0017
IV.	1.2672	—0.0045
V.	1.2717	0.

The quantity deduced as the result of each experiment of the present investigation is a ratio between the coefficients of viscosity of a gas at two different measured temperatures. As I have already shown,\* this ratio is expressible by the following equation :

$$y = \frac{\eta_t}{\eta_0} = \frac{R_2^4 \lambda_1}{R_1^4 \lambda_2} \cdot \frac{p_2^2 - p_3^2}{p_1^2 - p_2^2} \cdot \frac{1 + 3 A t}{1 + \alpha t},$$

where

$\eta_t$  = coefficient of viscosity of the gas at  $t^\circ$  C.

$\eta_0$  = " " " "  $0^\circ$  C.

$R_2$  = radius, and  $\lambda_2$  = length, of second capillary at  $t^\circ$ .

$R_1$  = radius, and  $\lambda_1$  = length, of first " "  $0^\circ$ .

$p_1$  = pressure of gas at entrance to first capillary.

$p_2$  = " " exit from first capillary, which is the same as that at entrance to second.

$p_3$  = pressure at exit from second capillary.

$t$  = temperature of second capillary.

$0^\circ$  = " first "

$A$  = coefficient of linear expansion of the glass.

$\alpha$  = mean coefficient of expansion of the gas between  $0^\circ$  and  $t^\circ$ , and under the pressure  $p_2$ .

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\* See references at end of paper.

Writing for brevity,

$$\frac{R_2^4 \lambda_1}{R_1^4 \lambda_2} = K, \text{ a constant;}$$

$$\frac{p_2^2 - p_3^2}{p_1^2 - p_2^2} = \phi(p), \text{ a function of } p;$$

and

$$\frac{1 + 3At}{1 + at} = \psi(t), \text{ a function of } t;$$

there results,

$$y = K \cdot \phi(p) \cdot \psi(t).$$

Differentiating this expression successively with respect to  $K, p_1, p_2, p_3, t, A$ , and  $a$ , then substituting for  $dy, dK, dp_1$ , &c.  $\Delta y, \Delta K, \Delta p_1$ , &c., and solving with respect to  $\Delta K, \Delta p_1$ , &c., the following expressions may be obtained:

$$\begin{aligned} \Delta K &= \frac{1}{\phi(p) \cdot \psi(t)} \cdot \Delta y \\ \Delta p_1 &= -\frac{(p_1^2 - p_2^2)^2}{2p_1(p_1^2 - p_2^2)} \cdot \frac{1}{K \cdot \psi(t)} \cdot \Delta y \\ \Delta p_2 &= \frac{(p_1^2 - p_2^2)^2}{2p_2(p_1^2 - p_2^2)} \cdot \frac{1}{K \cdot \psi(t)} \cdot \Delta y \\ \Delta p_3 &= -\frac{p_1^2 - p_2^2}{2p_3} \cdot \frac{1}{K \cdot \psi(t)} \cdot \Delta y \\ \Delta t &= -\frac{(1 + at)^2}{a} \cdot \frac{1}{K \cdot \phi(p)} \cdot \Delta y \\ \Delta A &= \frac{1 + at}{3t} \cdot \frac{1}{K \cdot \phi(p)} \cdot \Delta y \\ \Delta a &= -\frac{(1 + at)^2}{(1 + 3At)t} \cdot \frac{1}{K \cdot \phi(p)} \cdot \Delta y. \end{aligned}$$

From these, by inserting the proper numerical quantities taken from any suitable experimental result, may be computed the numerical values of  $\Delta K, \Delta p_1$ , &c., corresponding to any assumed value of  $\Delta y$ , and thus may of course be found the amount of change (or error) in  $K, p_1$ , &c., which would produce in  $y$  the assumed change (or error)  $\Delta y$ .

For the present purposes it is convenient to assume for  $\Delta y$  the same fractional value at all temperatures, and a convenient and suitable magnitude is  $\Delta y = 0.001 y$ . The following Table VIII. gives the

numerical values of  $\Delta K$ ,  $\Delta p$ ,  $\Delta t$ , &c., deduced from the experimental data of the second series for carbonic acid. The first column gives the tabular number of the measurements from which the data were taken.

TABLE VIII.  $\Delta y = 0.001 y$ .

No.	$t_2$ .	$\Delta K$ .	$\Delta p_1$ .	$\Delta p_2$ .	$\Delta p_3$ .	$\Delta t$ .	$\Delta A$ .	$\Delta a$ .	$\Delta H$ .
			mm.	mm.	mm.	° per ct.	per ct.	per ct.	
50	59.0	0.00104	-0.043	+0.028	-0.074	-0.33 -.56	+0.0000057 +70	-0.000021 .57	7.6
62	100.2	0.0010	-0.037	0.025	-0.077	-0.37 -.37	0.0000033 40	-0.000014 .40	
82	157.6	0.0010	-0.031	0.023	-0.084	-0.43 -.43	0.0000021 26	-0.000010 .27	
90	225.0	0.0010	-0.026	0.020	-0.092	-0.50 -.50	0.0000015 19	-0.0000082 .22	2.5

*Probable Effect on  $y$  of Instrumental Errors and Errors of Observation on the Values found and used for  $K$ ,  $p_1$ ,  $p_2$ , etc.*

Since the accuracy in the determination of  $K$  depends upon that of  $p_1$ ,  $p_2$ , and  $p_3$ , when both tubes are in ice, and thus under identical conditions, the latter quantities will be first considered.

I.  $\Delta p$ .

Constant errors in  $p_1$ ,  $p_2$ ,  $p_3$ , may be due to instrumental error of the barometer, or of the cathetometer which is used in the measurement of the mercury columns. Of course the fractional precision of the pressure measurements would be increased by increasing the driving pressure, but the possible deviation from the assumed laws of transmission of the gas through the tubes and of the increased liability to leakage with great rarefaction renders the use of a small pressure desirable. The cathetometer error has been reduced by the application of corrections determined for each decimeter of the scale by Prof. Wm. A. Rogers of Cambridge, and it was found not difficult to read the length of the mercury columns in the gauges with a probable error of less than 0.02 mm. The barometer was No. 835, made by James Green of New York, and had a scale of millimeters with vernier reading to 0.1 mm., and read by estimation as nearly to 0.01 as possible. Its instrumental error after careful refilling was determined by tests with the cathetometer and by indirect comparison with instruments of the U. S. Signal Service, and was probably under 0.3 mm., possibly considerably under that amount. As will be seen farther on, a constant error of this magnitude would have no sensible effect.

Further constant errors may be due to the following causes:—

1. Impure mercury in gauges. Carefully redistilled mercury only was employed. Any slight error from this source would be nearly eliminated through the use of the same mercury in the determination of both  $y$  and  $K$ .

2. Imperfect drying of the gas. The gas was retained over concentrated sulphuric acid from fifteen minutes upward before being passed through the drying tubes into the apparatus. These tubes were of more than 0.5 meter in length, and of such size that their contents would supply the apparatus with gas for upwards of a quarter of an hour. They contained anhydrous phosphoric acid, of which the surface was made greater by placing a portion of it upon a horizontal partition of wire gauze. The apparatus was dried as thoroughly as possible before the beginning of each day's observations, by repeated careful exhaustions, and by the transpiration of the dried gas during several hours.

3. Leakage into the apparatus in the portion where  $p_1$  was measured would not occur, as this pressure was always equal to or in excess of the external. Leakage into the space containing the gas under  $p_2$  would be fatal to accuracy, and was prevented at the necessary joints by placing as close together as practicable the ends of the glass tubes to be joined, wiring the rubber tube used as a connector firmly into place, and surrounding the tube with a bath of glycerine to preserve the rubber from drying and cracking. This arrangement showed upon careful tests no indication of leakage either of air or of moisture; and it is believed that such could not have occurred in amounts sufficient to vitiate the results to any appreciable extent, in view of the other precautions taken against accumulated moisture. Leakage into the space whose pressure was  $p_3$ , unless absurdly large in amount, could not cause error.

4. More or less complete clogging of the capillary tubes which would bring about any change in diameter was not indicated either by the course of the direct experiment, or by the check measurement of  $K$  made at several times.

5. Badly shaped connecting tubes would have introduced frictional resistance of an uncertain magnitude, but the tubes used were designed of suitable size to make the velocity through them so small as to require a motive pressure certainly less than 0.01 mm.

6. There arises naturally a question as to how far the pressure at which the gases are transpired affects the viscosity, a point which is discussed further at page 18 of this paper. That this effect is not

numerical values of  $\Delta K$ ,  $\Delta p$ ,  $\Delta t$ , &c., deduced from the experimental data of the second series for carbonic acid. The first column gives the tabular number of the measurements from which the data were taken.

TABLE VIII.  $\Delta y = 0.001 y$ .

No.	$t_2$ .	$\Delta K$ .	$\Delta p_1$ .	$\Delta p_2$ .	$\Delta p_3$ .	$\Delta t$ .	$\Delta A$ .	$\Delta a$ .	$\Delta H$ .
	°		mm.	mm.	mm.	° per ct.	per ct.	per ct.	
50	59.0	0.00104	-0.043	+0.028	-0.074	-0.33 -56	+0.0000057 +70	-0.000021 .57	7.6
62	100.2	0.0010	-0.037	0.025	-0.077	-0.37 -37	0.0000033 40	-0.000014 .40	
82	157.6	0.0010	-0.031	0.023	-0.084	-0.43 -43	0.0000021 26	-0.000010 .27	
90	225.0	0.0010	-0.026	0.020	-0.092	-0.50 -50	0.0000015 19	-0.0000082 .22	2.5

*Probable Effect on  $y$  of Instrumental Errors and Errors of Observation on the Values found and used for  $K$ ,  $p_1$ ,  $p_2$ , etc.*

Since the accuracy in the determination of  $K$  depends upon that of  $p_1$ ,  $p_2$ , and  $p_3$ , when both tubes are in ice, and thus under identical conditions, the latter quantities will be first considered.

I.  $\Delta p$ .

Constant errors in  $p_1$ ,  $p_2$ ,  $p_3$ , may be due to instrumental error of the barometer, or of the cathetometer which is used in the measurement of the mercury columns. Of course the fractional precision of the pressure measurements would be increased by increasing the driving pressure, but the possible deviation from the assumed laws of transmission of the gas through the tubes and of the increased liability to leakage with great rarefaction renders the use of a small pressure desirable. The cathetometer error has been reduced by the application of corrections determined for each decimeter of the scale by Prof. Wm. A. Rogers of Cambridge, and it was found not difficult to read the length of the mercury columns in the gauges with a probable error of less than 0.02 mm. The barometer was No. 835, made by James Green of New York, and had a scale of millimeters with vernier reading to 0.1 mm., and read by estimation as nearly to 0.01 as possible. Its instrumental error after careful refilling was determined by tests with the cathetometer and by indirect comparison with instruments of the U. S. Signal Service, and was probably under 0.3 mm., possibly considerably under that amount. As will be seen farther on, a constant error of this magnitude would have no sensible effect.

Further constant errors may be due to the following causes:—

1. Impure mercury in gauges. Carefully redistilled mercury only was employed. Any slight error from this source would be nearly eliminated through the use of the same mercury in the determination of both  $\gamma$  and  $K$ .

2. Imperfect drying of the gas. The gas was retained over concentrated sulphuric acid from fifteen minutes upward before being passed through the drying tubes into the apparatus. These tubes were of more than 0.5 meter in length, and of such size that their contents would supply the apparatus with gas for upwards of a quarter of an hour. They contained anhydrous phosphoric acid, of which the surface was made greater by placing a portion of it upon a horizontal partition of wire gauze. The apparatus was dried as thoroughly as possible before the beginning of each day's observations, by repeated careful exhaustions, and by the transpiration of the dried gas during several hours.

3. Leakage into the apparatus in the portion where  $p_1$  was measured would not occur, as this pressure was always equal to or in excess of the external. Leakage into the space containing the gas under  $p_2$  would be fatal to accuracy, and was prevented at the necessary joints by placing as close together as practicable the ends of the glass tubes to be joined, wiring the rubber tube used as a connector firmly into place, and surrounding the tube with a bath of glycerine to preserve the rubber from drying and cracking. This arrangement showed upon careful tests no indication of leakage either of air or of moisture; and it is believed that such could not have occurred in amounts sufficient to vitiate the results to any appreciable extent, in view of the other precautions taken against accumulated moisture. Leakage into the space whose pressure was  $p_3$ , unless absurdly large in amount, could not cause error.

4. More or less complete clogging of the capillary tubes which would bring about any change in diameter was not indicated either by the course of the direct experiment, or by the check measurement of  $K$  made at several times.

5. Badly shaped connecting tubes would have introduced frictional resistance of an uncertain magnitude, but the tubes used were designed of suitable size to make the velocity through them so small as to require a motive pressure certainly less than 0.01 mm.

6. There arises naturally a question as to how far the pressure at which the gases are transpired affects the viscosity, a point which is discussed further at page 18 of this paper. That this effect is not

outside the limits of error of observation in this method is however shown by the groups of measurements of  $K$  at various pressures as given in experiments 26 to 38 on  $\text{CO}_2$ . These show that for pressures  $p_1 - p_2$ , as given in the subjoined table, varying from 159.7 to 54.9 mm., the mean values of  $K$  deduced differ at most by less than 0.14 per cent, and the difference is also not progressive in either direction, but irregular, the means for the extremes of pressure being precisely the same.

$p_1 - p_2$	$K$
159.7 mm.	1.0387
70.9	1.0373
61.9	1.0375
54.9	1.0386

In addition to this, the close agreement of the results of the first series on  $\text{CO}_2$  with those of the second series afford an important check upon the latter, since the former were made with wholly different measuring and heating apparatus, and at pressures from two to three times as great.

7. It should be here noted, that any unequal action at the entrance of the various tubes which might vitiate results obtained by any direct method are to a large extent eliminated by the differential method here used, and would probably enter, if at all, as errors of the second order of magnitude; also, as elsewhere stated, that the surface friction or slip of the gas over the walls of the tube would influence the results only in so far as it changed with the temperature, and would therefore probably be imperceptible.

*Variable errors* may enter from instrumental sources in readings of the barometer or of the cathetometer. Errors of observation in the measurement of the length of the mercury columns by use of the cathetometer would rarely exceed 0.02 mm.; but this amount is considerably less than the pressure changes which occurred in the average experiment. The barometer reading was also obtained with a deviation of less than 0.02 mm. as far as concerns errors of observation. To eliminate as far as possible progressive changes in  $p_1$ ,  $p_2$ , and  $p_3$  during the limits of time required for making a complete set of observations at any given temperature, a pair or more of readings of each was taken, symmetrically distributed in regard to time, so that the means should correspond to about the same instant, and thus be as nearly as possible equivalent to simultaneous observations. The order of readings in the most complete sets would thus usually be barometer, thermometer giving temperature  $t$  of bath, gauges  $A, B, C$ , temperature

$t$ , gauges  $C, B, A$  (reversing order on ends of column also), temperature  $t$ , barometer, and finally the readings of auxiliary thermometers for temperatures of gauges, etc.

In order to eliminate as far as possible any uncertainty in setting the cross-hairs of the telescope upon the true top of the mercury meniscus, a difficulty requiring special precaution when readings to 0.01 mm. are attempted, the device was adopted of placing about the tube a clasp with a dull black internal surface. This clasp was placed upon the tube above the mercury column, and was pushed down the tube until the plane of its lower edge was nearly tangent to the mercury meniscus, which then appeared black against a bright background otherwise secured for it. Another convenient method is to make the meniscus bright against a dark background, which is accomplished readily by placing behind the tube a piece of paper separated along a horizontal line into two portions, the upper of which is white, the lower black. When a reading is to be taken, this is adjusted at such a height that the black shall be just visible above the top of the meniscus. In both of these methods it is essential that care be taken that the adjusted black edge be not more than about one fifth of a millimeter above the top of the meniscus, as otherwise error may be introduced through mistaking the reflection of the line by the meniscus for the actual top of the meniscus.

Errors in observation of the height of the barometer affect  $p_1, p_2$ , and  $p_3$  by equal amounts in any given experiment. The effect of such errors will therefore be small, and its magnitude, given in the last column of the preceding table, may be demonstrated in the following manner. In the expression

$$y = K \cdot \frac{p_2^2 - p_3^2}{p_1^2 - p_2^2} \cdot \psi(t)$$

may be inserted  $p_1 = H + c$ ,  $p_2 = H + b$ ,  $p_3 = H + a$ , where  $H$  is the barometric reading and  $c, b$ , and  $a$  are the gauge readings, at entrance, middle, and exit of the apparatus. Thus,

$$y = K \cdot \frac{b-a}{c-b} \left( 1 + \frac{a-c}{2H+c+b} \right)$$

$$\therefore \frac{dy}{dH} = -K \cdot \psi(t) \cdot \frac{a-b}{b-c} \cdot \frac{2(a-c)}{(2H+b+c)^2}$$

$$\therefore \Delta H = -\frac{c-b}{b-a} \cdot \frac{(2H+b+c)^2}{2(a-c)} \cdot \frac{1}{K \cdot \psi(t)} \cdot \Delta y.$$

As shown by the number deduced from this expression and given in the table, the value of  $\Delta H$  for  $\Delta y = 0.1$  per cent will be at least 2 mm. throughout the range of these measurements. Also when it is considered that constant barometric errors, since they enter with nearly the same magnitude and effect, but with opposite signs, in the determinations of  $K$  and of  $y$ , become inappreciable in effect when not amounting to several millimeters. That the value of  $\Delta H$  is so large will be seen, on inspection of the foregoing differential, to be due in part to the small value of the differences of initial and final pressures used in these experiments.

An inspection of measurements 26 to 38 of Table VI. will show that the average deviation in these determinations of  $K$  is 0.2 per cent. The average deviation in  $K$  which could come from the above-mentioned sources will be seen, however, to be less than 0.2, probably as small as 0.1 per cent, since  $K$  as measured is a function of  $p_1$ ,  $p_2$ , and  $p_3$  only. It thus appears probable that the assumed precision in the instrumental measurement of the pressures is not far in error.

Among other sources of variable error are:—

1. Irregular action of the aspirator causing more or less irregular changes in the amount of pressure at the exit of the gas, i. e. corresponding to  $p_3$ . Fluctuations of this sort would of course be felt at once on the gauge, but the corresponding adjustment of  $p_2$  would require some time, as it would require the transpiration of a definite amount of gas from the  $p_2$  space to the  $p_3$  space. By the use of the regulator which I have devised for the purpose, and which has been already described at page 5, it has been found feasible to keep the pressure constant within a millimeter during a whole day's experimenting, while the water pressure would run from 20 to 35 pounds at frequent intervals. And, as will be seen from an inspection of the values of  $p_3$  given in the tables, the pressure during a series of half a dozen experiments frequently remained constant within 0.2 or 0.3 mm. In a single experiment a change of 0.2 mm. was rare, the average being under 0.1 mm., including errors of reading by the cathetometer. It is thus evident, I think, that this irregularity in  $p_3$ , which is of the nature of an accidental error, since it may be of any magnitude and of either sign, would on the average introduce into  $y$  or  $K$  a deviation not exceeding 0.2 per cent, and probably less than that, and is therefore but little greater in its effect than other sources of accidental error already mentioned.

2. Owing to the want of perfect constancy in the temperature of the oil-bath, and to a slight opportunity for irregularity in the heating

of the conducting tubes at the point of entrance to the bath, the pressure  $p_2$  as measured at any instant might not correspond precisely with the temperature,  $t$ , observed at the same instant, since time would be required for the pressure to adjust itself by an increase or decrease of transpiration. This would, of course, slightly vitiate the result, and the amount of the effect would naturally increase with the temperature. Being a variable error, it would be partially eliminated by multiplied observations. An inspection of the records of readings giving  $p_2$  shows that the average deviation of the pairs of readings taken in the same experiment at any given temperature increases nearly as the temperature from 0.03 mm. at  $20^\circ$  to about 0.1 mm. at  $200^\circ$  C. This in connection with the column headed  $\Delta p_2$  in Table VIII. demonstrates that these observed variations in  $p_2$  were capable of producing average variable errors in  $y$  of from 0.1 per cent to 0.5 per cent, according to the temperature.

If the average deviation of the various groups of determinations of  $\eta_t : \eta_0$  in Table VI. be compared with the corresponding numbers in the table of errors, it will be seen that observed percentage deviations increase with the temperatures, while the precision required in the instrumental measurements increases much less rapidly in any case, in some cases not at all. Also the observed deviations are considerably greater than can be due to instrumental errors, including the thermometer. It seems to be thus indicated that this unequal or irregular heating is probably a correct explanation of the observed variations in  $p_2$ , and is one of the most prominent sources of error in this investigation, though at the same time one which might readily be removed by modifications of the apparatus which should lead to the maintenance of more constant temperatures of the bath, and to the elimination of any irregular heating of parts of the tube.

3. Errors in the determination of the temperatures  $t$  of the gauges would affect the values of  $p_1$ ,  $p_2$ , and  $p_3$ , through the reduction to  $0^\circ$ . Calling 0.00018 the coefficient of absolute expansion of mercury (the cathetometer-bar expansion was separately corrected), the correction to any observed gauge reading,  $l$ , would be, of course,  $C = 0.00018 \, l \, t$ , whence

$$\frac{dc}{dt} = 0.00018 \, l, \text{ and } \Delta t = \frac{\Delta c}{0.00018 \, l}.$$

Assuming  $\Delta c = 0.01$  mm., and  $l = 100$  mm.,

$$\Delta t = \frac{0.01}{0.00018 \times 100} = \frac{0.01}{0.018} = 0^\circ.55,$$

from which it is obvious that, as the longest column of mercury read in the gauges was about 100 mm., no appreciable error would be introduced into any of these columns through errors less than  $1^\circ$  in their temperature measurements. With the arrangement of screens used, and taking the temperature by means of a thermometer dipping into mercury in a tube of similar dimensions and similarly exposed to the gauge tubes, no error of this magnitude could enter into  $t$ . It is also obvious that, as the gauges were placed side by side and under similar conditions in every respect, the same proportionate error would be produced in each, and this would therefore be largely eliminated. Also, for the reason given in considering the effect of barometric errors, the effect of errors in the determination of its temperature would be wholly imperceptible, and indeed all temperature correction both of the gauges and of the barometer might be omitted without seriously affecting the accuracy of the results, for the reasons already shown, and because the temperatures of the mercury columns differed but a few degrees throughout the whole research.

## II. $\Delta K$ .

*Constant errors* in the determination of  $K$  may arise from any of the sources of error in measurement of  $p_1$ ,  $p_2$ , and  $p_s$ , just discussed, which can occur under the conditions which hold during the determination of  $K$ . These conditions have already been described in detail, and it has been shown that

$$K = \frac{p_1^2 - p_2^2}{p_2^2 - p_s^2},$$

when both capillaries are at the same temperature, conveniently that of melting ice. By the method used in a previous paragraph on variable barometric errors, it may be shown that a constant error even as great as 1 cm. would have an imperceptible effect on  $K$ , and this effect would be counterbalanced and eliminated by a similar and opposite effect of this error in measurements taken with the same barometer to determine  $y$ . To a less extent the same is true of constant errors of the cathetometer scale, and it may be asserted that both of these sources of error are practically eliminated from the results of this investigation. Further sources of constant error have been sufficiently discussed in the paragraphs I. 1-7, and it should be added that, in the packing of ice about the tubes, particular care was used, not only to obtain thorough contact and surrounding at first, but to see that this was maintained.

The *variable errors* attending the determination of  $K$  are those affecting  $p_1$ ,  $p_2$ , and  $p_3$ , and already discussed; and from the measurements of Table VI. just referred to, it appears that the variable errors arise about equally from instrumental measurements and from fluctuations in  $p_3$ .

### III. $\Delta A$ .

As shown by the column headed  $\Delta A$  in the tables, the accuracy necessary in the value of  $A$ , the coefficient of linear expansion of glass used in the computations, increases as the temperature rises, an error of 0.1 per cent in  $y$  corresponding, however, to an error of 20 per cent in  $A$  at the highest temperature attained. The value of  $3A$  used was as follows:—

At	$3A$ .	At	$3A$ .
0°	0.0000245	120°	0.0000266
40°	251	160°	275
80°	258	200°	284

These values were selected as corresponding quite closely to the probable change of the coefficient with change of temperature. The absolute value from 0° to 100° is based on measurements made on the same tube used, but the variation with the temperature was not measured. The error in this coefficient at 100° cannot, I think, exceed five per cent, and is not likely to reach that amount; and a consideration of the results obtained by many observers, besides those which I have myself made on similar kinds of glass, renders it certain that the value of  $3A$  at 200° cannot be much more in error than at 100°. Even had a constant coefficient been employed throughout, its error introduced into  $A$  could hardly have exceeded 15 per cent at any temperature, and had this coefficient been arbitrarily assumed from the results of other observers, an error exceeding 20 per cent would have been unlikely. Since the value of  $\Delta A$  in Table VIII. is 19 per cent at 225°, it appears that, with the values used, the results of the computations of  $y$  cannot have been sensibly in error from this source, even at the highest temperatures attained.

### IV. $\Delta a$ .

The most important quantity whose value is necessarily assumed in the computation of  $y$  is the coefficient of expansion of the gas used. This quantity and the temperature of transpiration, as may be seen from the columns headed  $\Delta a$  and  $\Delta t$ , or from the expression giving  $y$ ,

affect the value of  $y$  to an equal extent, and the two must be determined with a precision ranging from 0.57 per cent at  $60^\circ$  to 0.22 per cent at  $225^\circ$ , in order that each shall produce in  $y$  an error of less than 0.1 per cent. It is well known that the value of  $a$  for all gases changes with the pressure and temperature under which they expand. In the case in hand, the gas expands under the constant pressure  $p_2$  from the temperature  $0^\circ$  of the first capillary, to that  $t$  of the second. The experiments of Regnault furnish the best data for this coefficient, and I have adopted his figures without reducing them for the corrected value of the expansion of mercury, as the small change which would be necessary would not sensibly affect my results. Regnault gives as the coefficient of expansion of carbonic acid under constant pressure

$$\begin{array}{ll} \text{At } 760 \text{ mm.} & 100 a = 0.37099 \\ \text{" } 2520 \text{ " } & \text{" } = 0.38455 \end{array}$$

Although the function connecting the pressure and coefficient of expansion is unknown, yet simple extrapolation from these data gives values of  $a$  of sufficient relative precision for the present results, as the total variation of  $a$  within the range of  $p_2$  used is only about 0.12 per cent. The values actually used are given in the tables of experimental data, so that the general effect of this correction can there be noticed, and the data are sufficiently complete to allow a recalculation with other values if desirable. It will be seen here also, as in the value of  $A$ , the change in the coefficient is so small as to produce effects of less than 0.1 per cent if neglected altogether, but the retention of both favors the elimination of accumulated systematic error in  $y$  as a function of  $t$ . For this reason, a similar precaution has been taken in the computations for air, although in that case it is even less necessary.

#### V. $\Delta t$ .

The precision necessary in the measurement of  $t$ , the temperature of the second capillary, is shown in the column headed  $\Delta t$  in Table VIII.

1. As this investigation was aiming at the determination of the change of rate of variation of the viscosity with the temperature, and as this change was known to be small, it seemed of special importance that all precautions should be taken to eliminate systematic errors. And as thermometric measurements, even when conducted with more than ordinary care, are particularly liable to such errors, especial atten-

tion was devoted to this branch of the work. The precision obtained in the thermometry was doubtless greater than was necessary to correspond to that obtained in other parts of the determination of  $y$ , especially below  $60^{\circ}$ ; but it is doubtful if a satisfactory elimination of constant errors could have been obtained with any less care.

The investigations on thermometry which I have made, and still have under way, will be discussed here only in their relation to the measurements given in this paper. The important problem of how far the mercurial thermometer is available as a convenient representative (proxy) for the air thermometer at temperatures up to  $300^{\circ}\text{C.}$ , and under what conditions and methods it shall be so used, does not enter to any considerable extent into the work in hand, on account of the comparatively small degree of accuracy required in my measurements, even at the highest temperature ( $225^{\circ}$ ) used. The results which I have already obtained in this direction I hope to supplement by enough other material of the same nature to render the whole of sufficient value to be given by itself at some future time.

All the thermometric readings were taken with the bulb immersed in the oil-bath around the second capillary to a depth of about two inches. Above this point, the projecting stem was surrounded by a thin-walled glass tube, closed at the bottom by a rubber stopper through which the thermometer stem passed, and filled with water or glycerine, according to the temperature of the oil. This stem bath was stirred by a vertically moving stirrer, and its temperature was determined at one or more points, according to the length of the mercury column enclosed, by one or more auxiliary thermometers.

The readings were properly corrected for calibration error (except in the case of the Baudin normals, which were found by calibration to be accurate to two or three tenths of a division), for temperature of exposed stem, for true value of unit of scale (error of fixed points), and for deviation from the air thermometer. Poggendorff's correction becomes unnecessary where the mercurial thermometer, as in this work, is compared with the air thermometer direct, and all readings are reduced to that standard.

The thermometers used were respectively, one by Casella of London, No. 32378, and two by Baudin of Paris, Nos. 7335 and 7789. The following table gives the description of these, and of several others to be referred to later.

TABLE X.

Mark.	Approx. Length in cm.	Range.	Graduation.	Length occupied by 1° C.	Maker.	When made.	Owner.
7335	46	$\overset{\circ}{100}$ to $\overset{\circ}{200}$	$\overset{\circ}{0.1}$ C.	cm. 0.5	Baudin.	October, 1878.	S. W. Holman.
7789	40	100 to 200	0.2 C.	.....	Baudin.	.....	S. W. Holman.
32378	46	-15 to 110	0.2 C.	0.32	Casella.	Kew Register, 1873, -4, -8.	S. W. Holman.
6163	50	-6 to 40	mm.	0.9	Baudin.	1876-77.	Physical Laboratory, Johns Hopkins University.
7334	61	0 to 100	$\overset{\circ}{0.1}$ C.	0.5	Baudin.	October, 1878.	S. W. Holman.
Kew 104	66	-21 to 103	0.5 F.	0.46	Welch.	July, 1853.	Professor Barker, University of Pennsylvania.
Geissler	45	-3 to 102	0.1 C.	0.38	Geissler.	(?)	Chemical Laboratory, Johns Hopkins University.
368	48	Arbitrary equal volumes. About 0 to 100	Arbitrary equal volumes. } Arbitrary equal volumes. } $1^{\circ} 0$ F.	0.32	Fastré.	1851.	Professor Gibbs, Harvard College.
376	48	Arbitrary equal volumes. About 0 to 100		0.31	Fastré.	1851.	Professor Gibbs, Harvard College.
3235	40	32 to 212		0.16	Casella.	(Quite old.)	Harvard College Observatory.

It is always somewhat unfortunate, but usually unavoidable, to have the stem of the thermometer at a temperature lower than that of the bulb, and the correction from this cause increases about as the square of the temperature of the bulb. Among the discussions of the methods of correction for this error may be cited those of Kopp, Regnault, Holtzman, and, more recently, Wüllner\* and Mills.† After a careful experimental trial and consideration of these, it appeared to me that, for the present purposes, results fully equal to the requirements would be obtained by the use of a stem bath as above described.

Let  $s$  = mean temperature of this bath.

$t$  = actual temperature of bulb (to be determined).

0.000156 = coefficient of apparent expansion of mercury in glass.

$n$  = length of mercury column in units of the scale graduation at temperature  $s$ .

$r$  = direct reading of thermometer corrected for calibration error.

Then

$$t = r + 0.000156 (t - s)n,$$

or approximately

$$t = r + 0.000156 (r - s)n,$$

\* Lehrbuch der Experimental-Physik, iii. 312.

† Proc. Royal Soc. Edinburgh, xxix. 569.

since  $t = r$  very nearly. When, however,  $t - r$  becomes sufficiently large, the value of  $t$  as computed by the second expression must be considered as a first approximation only, and a second or third must be computed.

Without entering into the further discussion of thermometry which I have made, a portion of which was presented in a paper (unpublished) read at the Boston Meeting of the American Association for the Advancement of Science in 1880, I will assert that the errors in my thermometric work are below the values assigned to  $\Delta t$  in Table VIII.

In order to determine the deviation of the mercurial thermometers used in my measurements from the air thermometer, a direct comparison was made of these and several others, the results of which possess some interest, and will be here given.

Through the kindness of Prof. H. A. Rowland, to whom I would here express my sincere thanks for his courtesy and assistance, and by an appropriation granted by the Rumford Committee of the American Academy, I was enabled to visit Baltimore in January, 1879, and to make, in co-operation with Prof. Rowland, some thermometric comparisons, using an apparatus designed by him.

The method and apparatus for comparisons at temperatures below  $100^{\circ}$  C. were those described and discussed in full by Prof. Rowland in his valuable memoir on the Mechanical Equivalent of Heat.\* It is unnecessary to reproduce the description here further than to say that a water bath was used in the apparatus, that the whole thermometer was immersed, and that in the discussion of the accuracy of the apparatus Prof. Rowland writes, † "From this table it would seem that there should be no difficulty in determining the  $40^{\circ}$  point on the air thermometer to at least 1 in 2000; and experience has justified this result." It is quite possible, however, that the result obtained in my comparison was not of quite as high precision as this, but it did not fall far short.

On two successive days a group of four thermometers was compared with the air thermometer, with the results shown in the two following tables. Thermometer Baudin 6163, whose error had already been carefully studied by Prof. Rowland, was included in both series. Table IX., on page 38, gives the complete description of the various instruments. Casella 32378 was used in my measurements below  $100^{\circ}$ . It is a fairly good instrument, but decidedly inferior to any of

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\* These Proceedings, June, 1879, vol. xv. pp. 77 *et seq.*

† Ibid., p. 99.

the Baudin thermometers, both from its quite considerable calibration error, which is irregular between the  $95^{\circ}$  and  $100^{\circ}$  points, and from the lack of the calibration chamber at the top, as well as from the general form of the tube and bulb. The Kew register was also obtained, but was not used, as it was given only to  $0^{\circ}.1$ , i. e. half-divisions of the scale, and corresponds neither with the result of the comparison between Kew Standard No. 104, as given below, with the ascertained calibration error, nor with the air thermometer error. The pair of Fastré tubes, kindly lent for the comparison by Dr. Wolcott Gibbs of Harvard University, were of special interest, as being probably nearly identical with the crystal glass used by Regnault and calibrated by the method employed by him, Fastré being the maker of many of Regnault's thermometers.

The chief special points of interest in the results of these comparisons are indicated by Prof. Rowland at the place cited, and I will allude here only to the fact that all of the mercurial thermometers used in this study appear to read higher than the air thermometer below  $100^{\circ}$ .

TABLE X.

Air Thermometer.	Original Readings.					Reduced Readings.				
	6163 Baudin.	7334 Baudin.	Kew Stand- ard No. 104.	32378 Casella.	Geissler.	6163 Reduced to Air Thermometer.	7334 Baudin.	Kew Stand- ard No. 104.	32378 Casella.	Geissler.
$0^{\circ}$	*58.83	—0.11	32.68	+0.20	+0.69	$0^{\circ}$	$0^{\circ}$	$0^{\circ}$	$0^{\circ}$	$0^{\circ}$
†0.43	63.5	....	33.60	0.71	....	0.52	....	0.52	0.51	....
6.08	113.0	....	43.65	6.33	....	6.08	....	6.11	6.12	....
12.68	171.55	12.59	55.47	12.91	13.42	12.65	12.73	12.68	12.70	12.82
20.49	242.0	20.48	69.55	20.77	21.29	20.49	20.63	20.57	20.56	20.74
24.55	278.8	24.50	76.90	24.80	25.33	24.54	24.66	24.61	24.59	24.81
29.51	323.9	29.49	85.88	29.80	30.32	29.52	29.66	29.61	29.58	29.83
39.45	413.1	39.43	103.72	39.76	40.22	39.47	39.62	39.53	39.54	39.80
39.15	410.7	39.15	103.23	39.48	39.98	39.20	39.34	39.26	39.26	39.56
51.17	....	51.10	124.84	51.49	51.83	....	51.32	51.29	51.26	51.49
61.12	....	61.05	142.73	61.47	61.69	....	61.29	61.24	61.23	61.41
70.74	....	70.57	159.87	71.00	71.14	....	70.83	70.78	70.76	70.92
80.09	....	79.74	176.50	80.31	80.25	....	80.02	80.04	80.06	80.10
80.39	....	80.15	177.23	80.74	80.66	....	80.43	80.44	80.49	80.51
89.95	....	89.63	194.35	90.22	90.11	....	89.93	89.97	89.97	90.03
89.92	....	89.59	194.22	90.18	90.06	....	89.89	89.90	89.93	89.98
100.00	....	99.69	212.37	100.06	99.32	....	100.00	100.00	100.00	100.00

\* The original readings in ice were 58.68 and 58.45, to which .15 was added to allow for pressure of water in the comparator. This, of course, gives the same final result as if .15 were subtracted from each of the other temperatures. No correction was made to the others.

† Probably some error of reading.

TABLE XI.

Air Ther- mometer.	Original Readings.					Reduced Readings.				
	6163 Baudin.	376 Fastré.	7316 Baudin.	368 Fastré.	3235 Casella.	6163 Reduced to Air Ther- mometer.	376 Fastré.	7316 Baudin.	368 Fastré.	3235 Casella.
0.	*58.60	111.3	-0.23	87.6	32.80	0.	0.	0.	0.	0.
3.67	90.7	130.0	....	106.25	39.35	3.61	3.64	....	3.64	3.65
11.55	161.6	170.9	11.40	147.2	53.70	11.56	11.60	11.64	11.62	11.63
20.72	243.7	217.9	20.59	194.2	70.15	20.70	20.75	20.84	20.80	20.79
32.19	347.4	276.9	32.09	253.2	90.80	32.17	32.24	32.34	32.28	32.29
39.36	411.85	313.85	39.26	290.1	103.68	39.36	39.43	39.52	39.48	39.45
50.71	....	372.0	50.57	348.2	123.65	....	50.75	50.84	50.80	50.57
60.10	....	420.0	59.92	396.45	140.80	....	60.10	60.19	60.21	60.12
73.82	....	490.6	73.59	466.85	165.68	....	73.84	73.87	73.93	73.97
86.50	....	555.25	86.16	531.22	188.20	....	86.48	86.51	86.56	86.56
....	....	550.2	85.21	525.95	186.42	....	85.45	85.50	85.45	85.51
100.00	....	624.93	99.70	600.58	212.45	....	100.00	100.00	100.00	100.00

The comparisons above 100° were of rather more importance than those below for the purpose of the present investigation. For this work the newly constructed apparatus designed by Prof. Rowland was put in use for the first time.

It consists of a massive copper vessel of circular section, having inner dimensions of 18.5 cm. depth and 23 cm. diameter, and with walls and bottom 1.2 cm. thick. Upon the carefully turned flange which forms the upper edge of the walls is bolted a correspondingly heavy circular copper plate, a projection from which enters a short distance into the vessel. From the middle of this plate, and cast upon it, rises a heavy copper bar of 10 cm. by 6 cm. cross-section outside, and 55 cm. high, but containing a vertical channel in its broader front face having a depth of 3.5 cm. and a width of 8 cm. Sheet-iron covers of suitable length and about 4 cm. width are provided to close those portions of the front of this channel which should be closed during the work. The cylindrical vessel up to the flanges is placed within a sheet-iron casing, from which rises at the back a sheet-iron outlet pipe which extends upward along the back of the channelled bar to its top. The heated gases escaping through this flue from the Bunsen burner placed beneath the copper vessel heat the bar to any desired temperature, regulation being had by means of inlet valves admitting cool air at the base of the flue.

\* See note to preceding table.

the Baudin thermometers, both from its quite considerable calibration error, which is irregular between the 95° and 100° points, and from the lack of the calibration chamber at the top, as well as from the general form of the tube and bulb. The Kew register was also obtained, but was not used, as it was given only to 0°.1, i. e. half-divisions of the scale, and corresponds neither with the result of the comparison between Kew Standard No. 104, as given below, with the ascertained calibration error, nor with the air thermometer error. The pair of Fastré tubes, kindly lent for the comparison by Dr. Wolcott Gibbs of Harvard University, were of special interest, as being probably nearly identical with the crystal glass used by Regnault and calibrated by the method employed by him, Fastré being the maker of many of Regnault's thermometers.

The chief special points of interest in the results of these comparisons are indicated by Prof. Rowland at the place cited, and I will allude here only to the fact that all of the mercurial thermometers used in this study appear to read higher than the air thermometer below 100°.

TABLE X.

Air Thermometer.	Original Readings.					Reduced Readings.				
	6163 Baudin.	7334 Baudin.	Kew Stan- dard No. 104.	32378 Casella.	Geissler.	6163 Reduced to Air Thermometer.	7334 Baudin.	Kew Stan- dard No. 104.	32378 Casella.	Geissler.
0.	*58.83	-0.11	32.68	+0.20	+0.69	0.	0.	0.	0.	0.
10.43	63.5	....	33.60	0.71	....	0.52	....	0.52	0.51	....
6.08	113.0	....	43.65	6.33	....	6.08	....	6.11	6.13	....
12.68	171.55	12.59	55.47	12.91	13.42	12.65	12.73	12.68	12.70	12.82
20.49	242.0	20.48	69.55	20.77	21.29	20.49	20.63	20.57	20.56	20.74
24.55	278.8	24.50	76.90	24.80	25.33	24.54	24.66	24.61	24.59	24.81
29.51	323.9	29.49	85.88	29.80	30.32	29.52	29.66	29.61	29.58	29.83
39.45	413.1	39.43	103.72	39.76	40.22	39.47	39.62	39.53	39.54	39.80
39.15	410.7	39.15	103.23	39.48	39.98	39.20	39.34	39.26	39.26	39.56
51.17	....	51.10	124.84	51.49	51.83	....	51.32	51.29	51.26	51.49
61.12	....	61.05	142.73	61.47	61.69	....	61.29	61.24	61.23	61.41
70.74	....	70.57	159.87	71.00	71.14	....	70.83	70.78	70.76	70.92
80.09	....	79.74	176.50	80.31	80.25	....	80.02	80.04	80.06	80.10
80.39	....	80.15	177.23	80.74	80.66	....	80.43	80.44	80.49	80.51
89.95	....	89.63	194.35	90.22	90.11	....	89.93	89.97	89.97	90.03
89.92	....	89.59	194.22	90.18	90.06	....	89.89	89.90	89.93	89.98
100.00	....	99.69	212.37	100.06	99.32	....	100.00	100.00	100.00	100.00

\* The original readings in ice were 58.68 and 58.45, to which .15 was added to allow for pressure of water in the comparator. This, of course, gives the same final result as if .15 were subtracted from each of the other temperatures. No correction was made to the others.

† Probably some error of reading.

TABLE XI.

Air Ther- mometer.	Original Readings.					Reduced Readings.				
	6163 Baudin.	376 Fastré.	7316 Baudin.	308 Fastré.	3235 Casella.	6163 Reduced to Air Ther- mometer.	376 Fastré.	7316 Baudin.	308 Fastré.	3235 Casella.
0.	*58.60	111.3	-0.23	87.6	32.80	0.	0.	0.	0.	0.
3.67	90.7	130.0	....	106.25	39.35	3.61	3.64	....	3.64	3.65
11.55	161.6	170.9	11.40	147.2	53.70	11.56	11.60	11.64	11.62	11.63
20.72	243.7	217.9	20.59	194.2	70.15	20.70	20.75	20.84	20.80	20.79
32.19	347.4	276.9	32.09	253.2	90.80	32.17	32.24	32.34	32.28	32.29
39.36	411.85	313.85	39.26	290.1	103.08	39.36	39.43	39.52	39.48	39.45
50.71	....	372.0	50.57	348.2	123.65	....	50.75	50.84	50.80	50.57
60.10	....	420.0	59.92	396.45	140.80	....	60.10	60.19	60.21	60.12
73.82	....	490.6	73.59	466.85	165.68	....	73.84	73.87	73.93	73.97
86.50	....	555.25	86.16	531.22	188.20	....	86.48	86.51	86.56	86.56
....	....	550.2	85.21	525.95	186.42	....	85.45	85.50	85.45	85.51
100.00	....	624.93	99.70	600.58	212.45	....	100.00	100.00	100.00	100.00

The comparisons above 100° were of rather more importance than those below for the purpose of the present investigation. For this work the newly constructed apparatus designed by Prof. Rowland was put in use for the first time.

It consists of a massive copper vessel of circular section, having inner dimensions of 18.5 cm. depth and 23 cm. diameter, and with walls and bottom 1.2 cm. thick. Upon the carefully turned flange which forms the upper edge of the walls is bolted a correspondingly heavy circular copper plate, a projection from which enters a short distance into the vessel. From the middle of this plate, and cast upon it, rises a heavy copper bar of 10 cm. by 6 cm. cross-section outside, and 55 cm. high, but containing a vertical channel in its broader front face having a depth of 3.5 cm. and a width of 8 cm. Sheet-iron covers of suitable length and about 4 cm. width are provided to close those portions of the front of this channel which should be closed during the work. The cylindrical vessel up to the flanges is placed within a sheet-iron casing, from which rises at the back a sheet-iron outlet pipe which extends upward along the back of the channelled bar to its top. The heated gases escaping through this flue from the Bunsen burner placed beneath the copper vessel heat the bar to any desired temperature, regulation being had by means of inlet valves admitting cool air at the base of the flue.

\* See note to preceding table.

The bulb of the air thermometer is introduced into the middle of the copper vessel, and is surrounded by oil, which completely fills the vessel. The stem of the thermometer passes through a groove provided in the upper surface of the vessel. The mercurial thermometers are placed against the back of the vertical channel, with their bulbs projecting into the oil-bath to the level of the air thermometer bulb. The unoccupied space in the channel between the stems of the thermometers and the sheet iron front is filled with cotton wool or other similar substance, which may be removed at suitable points to take readings. Auxiliary thermometers are placed with the bulbs at various suitable heights along the stems of the other thermometers, and by means of them the temperature of the vertical bar, and thus of the thermometer stems, is maintained at a known temperature very nearly the same as that of the bath, so that the stem exposure correction becomes small and determinate. The massiveness and correspondingly high conductivity and calorific capacity of the whole vessel render it possible to maintain the temperature nearly uniform and constant during the time necessary for the thermometers to acquire the temperature of the bath and the readings to be taken. The oil-bath is thoroughly stirred by a sheet-iron stirrer moving vertically.

The air thermometer used was an imported instrument of the form described by Jolly.\* The glass of the bulb was supposed to be of the kind used by him, and the coefficient of expansion used in my computations was based on that which he has given, and was assumed, with sufficient accuracy for the present purposes, to be, —

$t^{\circ}$	Mean coeff. from $0^{\circ}$ to $t^{\circ}$ .
100	0.0000278
140	286
180	295
200	300
250	31
300	32

The mercurial columns were read by means of black hard-rubber clasps sliding upon the tubes, the scale being upon the surface of a glass mirror. Readings were taken to tenths of a millimeter. For the temperature reductions of the mercury columns it was assumed that the coefficient of apparent expansion of the glass scale was

$$\Delta = 0.000181 - 0.000009 = 0.000172,$$

---

\* Pogg. Ann. Jubelband (1874); Amer. Jour. Sci., vi. 591.

and that the scale was correct at  $0^{\circ}$  C., which was certainly quite nearly true. The value of the coefficient of expansion of air found with this apparatus was  $\alpha = 0.003679$ .

In February, 1879, I made a comparison of four thermometers, including Baudin 7335 and 6161, and two other thermometers of little value, at temperatures from  $100^{\circ}$  to  $250^{\circ}$  C., with the apparatus just described. The results were fairly good, but not entirely satisfactory. Later in the same year, Dr. E. H. Hall (then a student at Baltimore) made a similar series of comparisons, using Baudin thermometers Nos. 6161, 7315, 7325, and 7324. His results with No. 6161 differed somewhat from mine, owing chiefly to the progressive change in zero which attended this thermometer during my own use of it, as well as to something of the same change during his own measurements. The results as a whole agree fairly well, and I have deemed it best to average the corrections found on all the Baudin instruments of both series, and to use this average result as a correction to Baudin 7335, which I employed in my subsequent measurements. This seemed to me the safest course, because of the general agreement of all the Baudin thermometers used, and because more comparisons of 7335 could not be made at that time to eliminate the errors entering into a single series. That the table of errors thus obtained and given below is not all that might be desired is obvious, but I am disposed to believe that at  $200^{\circ}$  it is not in error by an amount exceeding  $0.5$ , and by a less amount at lower temperatures, thus introducing into  $y$  an error not exceeding  $0.1$  or  $0.2$  per cent.

TABLE XII.

DEVIATION OF BAUDIN No. 7335 FROM AIR THERMOMETER.

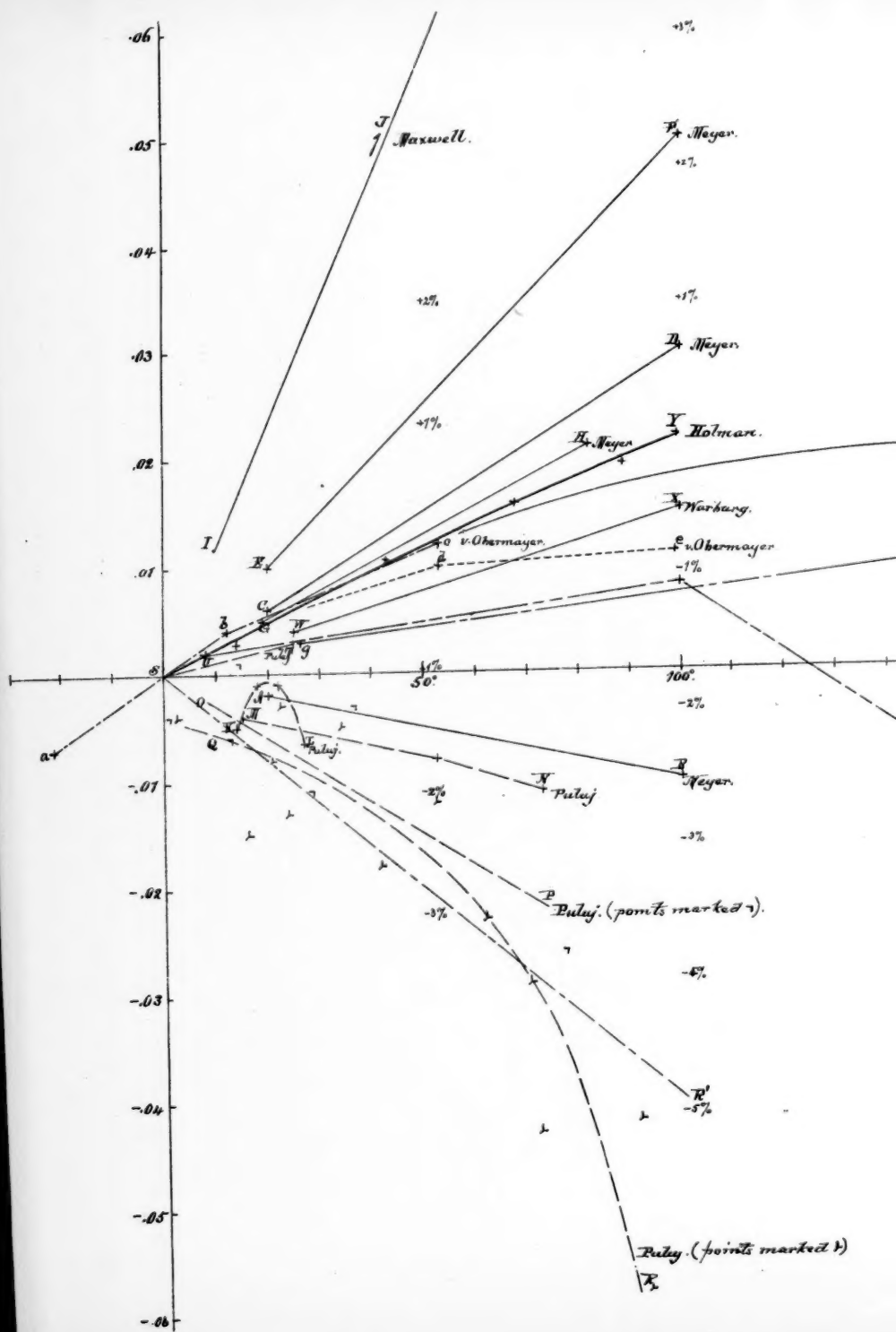
$\Delta t$ °	$\Delta$ °	$\Delta t$ °	$\Delta$ °
100	0.0	160	1.45
120	— 0.5	180	1.65
140	— 1.0	200	1.50

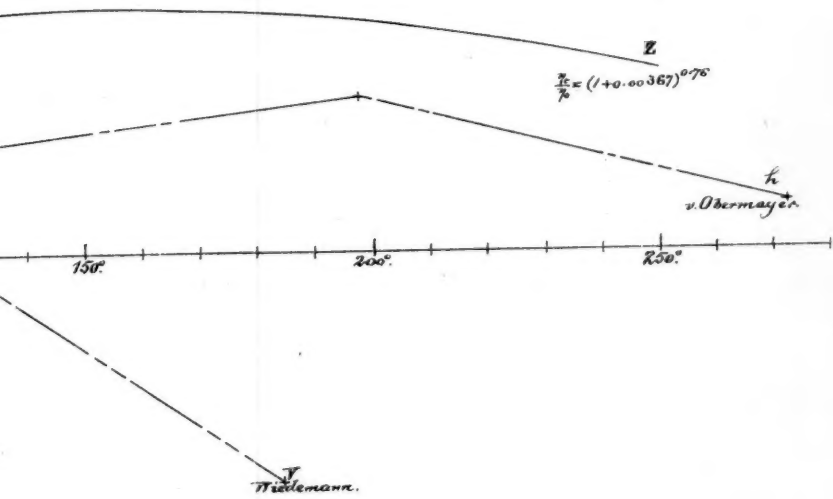
The measurements made at  $225^{\circ}$  were taken with Baudin No. 7789, and the correction to be applied to it was ascertained, by a comparison with No. 7335, to be  $+0.8$ .

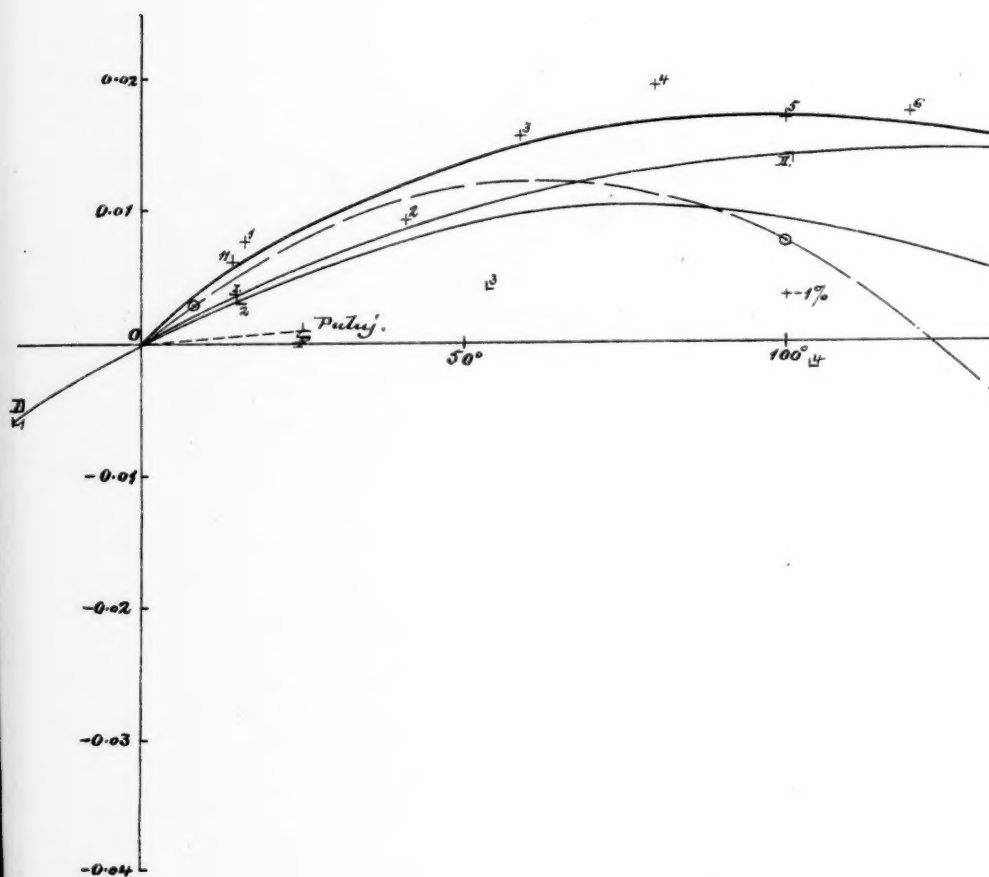
I have devised and had constructed an apparatus for air-thermometer corrections at high temperatures, and had hoped to be able to make a further series of comparisons of all thermometers used, but for reasons elsewhere stated the work is unfinished, and has no prospect of immediate completion.

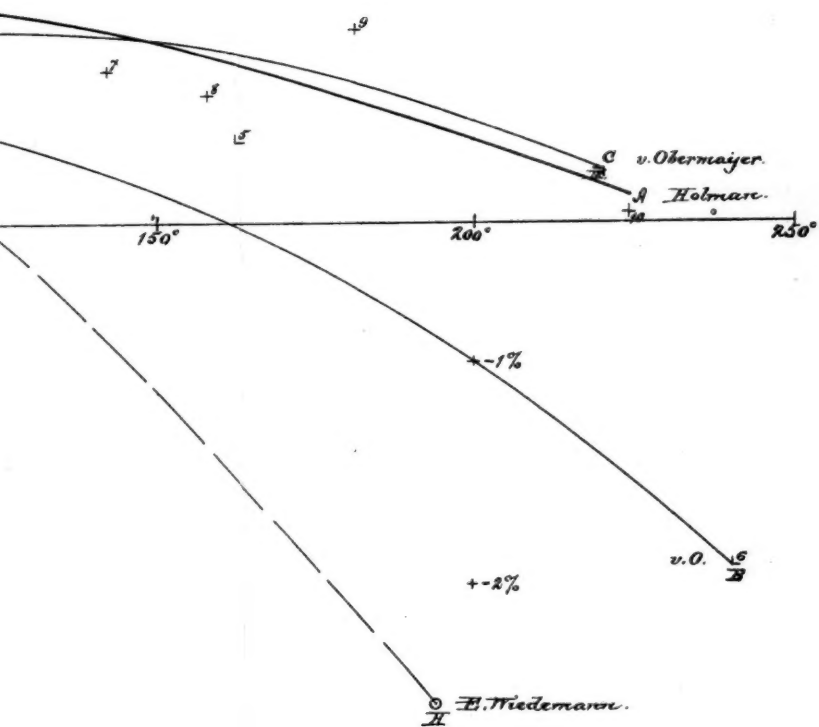














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## II.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY.XXI.—COMPARISON OF ALCOHOL THERMOMETERS  
BAUDIN 8208 AND 8209 WITH THE AIR THER-  
MOMETER AT LOW TEMPERATURES.

BY ANTHONY C. WHITE.

Communicated by S. W. HOLMAN, June 10, 1885.

THE results given in this paper were reached in a somewhat careful study of the alcohol thermometer made in the Physical Laboratory of the Institute of Technology during 1881-82. The study, though by no means exhaustive, developed some points of value which are here given. The comparison with the air thermometer agrees substantially with that published by Jolly.\*

The alcohol thermometers used were two centigrade tubes, made by Baudin, Paris, in 1880. They were precisely similar, and of the following dimensions: total length, 50 cm.; length of bulb, 4.5 cm.; length of  $1^{\circ}$  C., 0.28 cm.; divided to  $0^{\circ}.1$  C.; range from  $+35^{\circ}$  to  $-90^{\circ}$  C.

The air thermometer was of the Jolly type, but the mercurial columns were read by a cathetometer. Its bulb was of small size, diameter 3.48 cm., to insure a rapid equalization of the temperature within and without, and to allow the use of a small bath of liquid nitrous oxide.

The cathetometer was by Staudinger. Its scale was in millimeters with vernier reading directly to  $\frac{1}{20}$  mm. and by estimation to 0.01 mm. The scale errors had been determined by Prof. William A. Rogers of Harvard University, and corrections were applied. The barometer, by James Green, was of the Fortin type, and read to 0.002 inch. The scale and instrument errors had been previously determined.

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\* Pogg. Ann. Jubelband (1874).

The temperatures,  $T$ , by the air thermometer, were computed as described in Professor Rowland's paper on the Mechanical Equivalent of Heat.\* The numerical value of  $v$  was 0.80 cc.; of  $V$ , 20.21 cc. The thermometer was first filled with air dried by calcium chloride and concentrated sulphuric acid. The coefficient of expansion of this air was then measured several times. Six independent measurements gave values of  $a =$

0.003699	0.003699
3707	3702
3685	3702

Average = 0.003699

These results are sufficiently concordant in view of the small capacity of the bulb of the thermometer, but the average is nearly one per cent higher than the proper value, 0.003670. The cause of this deviation is unknown. It is possibly in part due to imperfect drying of the air. Its effect on the resulting temperature measurements will be small, however, since  $a$  and  $T$  are determined by the use of the same mass of air, and the moisture, if any were present, must have been in so small quantity as not sensibly to influence the results through condensation, etc. If the deviation be due to any undetected constant error, it will produce but little error in the temperatures obtained, since the air thermometer is used under essentially the same conditions for the determination of  $a$  and of  $T$ .

The vessel for holding the cold bath, or "freezing mixture," was composed of several concentric glass and metal vessels, the spaces between successive vessels being filled either with dry sawdust or with a freezing mixture, or with these alternating. The arrangement employed when the freezing mixture of salt and ice was used consisted of five concentric vessels. Between the outer and the second vessels was a space filled with sawdust. Between the second and third was a space of larger capacity than the former, which contained a mixture of salt and ice. Between the third and fourth vessels was another sawdust layer; and between the fourth and inner vessels, a second freezing mixture of salt and ice; while the inner vessel was filled with alcohol, in which the bulbs were immersed and which was thoroughly stirred. A suitable cover of several thicknesses of badly conducting material was provided for the whole. When the liquid nitrous oxide was used, the whole space between the third and a

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\* These Proceedings, June, 1879, vol. xv.

smaller interior glass vessel was packed with sawdust, the first outer bath of salt and ice being retained. Instead, however, of filling the innermost vessel with the liquid nitrous oxide alone, the space was first filled with fine copper turnings and filings. These occupied so much of the volume as considerably to reduce the amount of the liquid  $N_2O$  required, and at the same time by their good thermal conductivity tended to maintain a uniform temperature throughout the mass without stirring. The device was found very satisfactory in operation. The liquid  $N_2O$  was obtained by the rapid discharge of a cylinder somewhat highly charged with the gas. The cylinder was one of those in which this gas is commercially distributed for use as an anæsthetic, but was more highly charged than is usual.

In the comparison of the alcohol and air thermometers, the conditions were necessarily rather unfavorable for high precision, but the arrangements adopted are believed to have given mean results correct to  $0.5^\circ C.$ , or (probably) less at the lowest temperatures reached, as high a degree of precision as can be relied upon with the alcohol thermometer. The difficulty and expense of using a large bath of liquid nitrous oxide precluded the total immersion of the thermometer in the bath at low temperatures, and as it was thought desirable to work under the same conditions as to stem exposure at all temperatures, the same general arrangement was used throughout. The bulb and an inch or two of the capillary were therefore the only parts of the thermometers immersed, the remainder of the stem being surrounded by a thin glass tube of about an inch in diameter, filled with water, which, when properly stirred, rendered the temperature of the stem uniform, and measurable (by an auxiliary thermometer). The two alcohol thermometers passed side by side through the same stem bath, and had their bulbs nearly in contact with each other and with the air bulb in the cold bath.

The scale of the alcohol thermometers was supposed to be normal, i. e. of lines so spaced as to separate equal volumes of the capillary, and to give approximate degrees by direct reading. It was also supposed that the spacing of the degrees was determined by the use of ice, and by comparison with a standard mercurial thermometer at one or more temperatures, probably above  $0^\circ C.$ , or by some equivalent process, so that one degree of the scale at or near  $0^\circ C.$  corresponds as closely as may be with  $1^\circ C.$  as ordinarily defined on the mercurial thermometer, or, more precisely, with the degree as measured with the Baudin standard mercurial thermometer. It was obviously of no special interest, therefore, to study further the temperature value of

one division of the scale, although through the failure to do so the investigation lacks completeness.

The correction for the temperature difference between the stem and bulb, i. e. the "stem exposure correction," was made through the use of the customary expression,

$$n (T - t) k,$$

where

$T$  = the temperature of the bulb, in these measurements given by the air thermometer.

$t$  = the temperature of the exposed stem,

$n$  = the length expressed in degrees of the exposed alcohol column,

$k$  = the coefficient of apparent expansion of the alcohol in the glass of the thermometer.

The value of  $k$  was measured in two ways: first, by an independent study with the alcohol bulbs in ice and the projecting stems at measured temperatures; secondly, from the results in the comparison with the air thermometer at about  $0^{\circ}$  C. These gave results in substantial agreement, but the second method was considered more reliable, and likely to aid in eliminating constant errors in the comparison since made under the same conditions, and its value of  $k = 0.00091$  was adopted.

The readings of the thermometers in ice were taken at intervals, to follow the changes with age and usage, and the instruments were never raised to a temperature above that incidental to the manipulation. The zero point of 8209 rose from  $-0^{\circ}.18$  C., in October, 1880, to  $+0^{\circ}.16$  in April, 1882. The change in 8208 was probably about the same, but the data do not extend over the same time.

The following are the mean values obtained by averaging in suitable groups the eighty readings obtained in the comparison with the air thermometer.

Air Therm.	8208.	8209.	$\delta_8$ .	$\delta_9$ .	$\delta_9 - \delta_8$ .
$+ 0.72$	$+ 0.69$	$+ 0.69$	$-0.03$	$-0.03$	$0.00$
$- 2.06$	$- 2.00$	$- 2.00$	$+0.06$	$+0.06$	$0.00$
$- 6.86$	$- 6.68$	$- 6.63$	$0.18$	$0.23$	$0.05$
$-10.45$	$-10.08$	$-10.03$	$0.37$	$0.42$	$0.05$
$-16.37$	$-15.59$	$-15.47$	$0.78$	$0.90$	$0.12$
$-19.80$	$-18.80$	$-18.67$	$1.00$	$1.13$	$0.13$
$-37.94$	$-79.02$	$-78.46$	$8.92$	$9.48$	$0.56$

The first column gives the temperatures by the air thermometer, the second column the corrected readings by Baudin 8208, the third the corrected readings for 8209, the fourth the deviation of 8208 from the air thermometer, the fifth the same for 8209, and the sixth the differences between the two Baudin thermometers. In the series of eighteen comparisons which give the means corresponding to  $-87^{\circ}.94$  the average deviation of the single numbers giving the mean in the fourth or fifth columns was  $0^{\circ}.16$ .

For the sake of comparison, the figures published by Jolly are here appended.

Air Therm.	Alcohol.	$\delta$ .
$-6.32$	$-6.21$	$0.11$
$-11.02$	$-10.72$	$0.30$
$-15.25$	$-14.41$	$0.84$
$-19.29$	$-18.02$	$1.27$
$-79.44$	$-70.72$	$8.72$

## III.

## RESEARCHES ON THE COMPLEX INORGANIC ACIDS.

BY WOLCOTT GIBBS, M. D.,

*Rumford Professor in Harvard University.*

(Continued from Vol. XVIII p. 274.)

Communicated June 10, 1885.

## PHOSPHO-VANADATES.

THE existence of a compound of phosphoric and vanadic pentoxides appears to have been first recognized by Berzelius, who regarded it simply as a phosphate of vanadic oxide and ascribed to it the formula  $V_2O_5 \cdot 3 P_2O_5$ , vanadium being then supposed to have the atomic weight 61.5, so that its highest oxide would have the formula  $V_2O_5$ . Berzelius describes the supposed salt as lemon-yellow, crystalline, and slowly soluble in water. By dissolving together sodic phosphate and vanadate, adding nitric acid and evaporating at a gentle heat, he obtained a colorless solution which yielded a lemon-yellow salt in large grains made up of fine crystalline needles. For this compound, which he called phosphate of sodium and vanadic acid, he gave no formula. I shall endeavor to show that phosphoric and vanadic oxides unite in various proportions to form well-defined complex inorganic acids, strictly comparable with those which contain phosphoric and molybdic or tungstic oxides.

Phospho-vanadates are formed when alkaline vanadates are heated in contact with free phosphoric acid; when solutions of an alkaline phosphate are digested with vanadic acid or an acid vanadate; and when alkaline phosphates and vanadates are mixed in presence of a free acid, the conditions being, so far as I have observed, perfectly analogous to those which determine the formation of phospho-tungstates and phospho-molybdates. Phospho-vanadates of the heavy metallic oxides are formed when the divanadates of these oxides are boiled with solutions of alkaline phosphates or with phosphoric acid, and also when

the corresponding metallic phosphates are boiled with vanadic acid or acid vanadates. As a rule, the salts are beautifully crystalline, and have a yellow or orange-yellow color, passing in some cases to deep orange-red.

The general characters of the phospho-vanadates are as follows. The alkaline salts have a sulphur-yellow, and in some cases bright yellow color. They are crystalline and often present minute talcose shimmering scales. The relation of these salts to water is especially remarkable. A small quantity of water simply dissolves the phospho-vanadate with a yellow color; on adding more water, the solution gradually becomes orange, then orange-red, and finally deep red. Phosphoric acid is set free, and one or more new definite salts are formed, in which the proportion of the vanadic to the phosphoric oxide is largely increased. Precisely similar changes occur in the action of water upon arsenio-vanadates. When the deep red solutions are evaporated, the changes of color described occur again in the inverse order, and finally the original yellow salt is again obtained, though not always perfectly free from the higher compound. The facility with which the salts of this series are decomposed by water makes it often difficult to obtain them in a state of absolute purity, and renders the reactions with metallic salts uncertain as characteristics. When alkaline phospho-vanadates are evaporated with nitric acid, the base is in many cases entirely separated, and phospho-vanadic acid remains in solution and may separate in crystals. This separation of fixed base often takes place in presence of an excess of phosphoric acid alone. Solutions of alkaline phospho-vanadates appear to be partially reduced by dust or traces of organic matter with exceptional facility. In such cases the solutions take a more or less distinct greenish color, and phospho-vanadico-vanadates are formed. The solutions of these last salts are not very easily oxidized by bromine or nitric acid, and it is therefore advisable in preparing phospho-vanadates to avoid as much as possible the presence of reducing agents. Alkaline phospho-vanadates dissolve readily in hot solutions of acid tungstates and molybdates, forming orange or orange-red solutions, which yield in many cases beautiful crystalline phospho-vanadio-molybdates and phospho-vanadio-tungstates.

*Analytical Methods.* — The method usually adopted for the separation of vanadic and phosphoric oxides by means of ammoniac chloride may be successfully applied to the analysis of the phospho-vanadates. A small excess of ammonia is to be added to the solution of the salt, which is then to be heated until it becomes colorless. In this manner

we obtain a simple mixture of phosphate and metavanadate. Ammonic chloride is then to be added, and the analysis conducted in the usual manner. This method permits the separate determination of each of the pentoxides and so far offers an advantage. On the other hand, it only applies to salts with alkaline bases. It is far more convenient, and at least equally accurate, to determine the vanadium by titration with hypermanganate under appropriate conditions. The end reaction is usually well defined in a sufficiently dilute solution. The sum of the vanadic and phosphoric oxides may be accurately determined by precipitating the solution of the two pentoxides at a boiling heat by means of mercurous nitrate, adding mercuric oxide until a small but distinct excess is present so as to perfectly neutralize the free acid, and then boiling for a few minutes. Since the ignited mass of oxides retains mercuric oxide with some tenacity, it is best, after burning off the filter with a very free access of air, to add a weighed portion of sodic tungstate and ignite until a constant weight is obtained. When the process is carefully conducted, the fused mass contains all the phosphoric oxide and all the vanadium as pentoxide. Care should be taken to oxidize the whole of the vanadium to pentoxide as more certain. Any small quantity of dioxide present is however precipitated when an excess of mercuric oxide is present. This method applies to all salts or compounds containing oxides of phosphorus and vanadium. As regards the details of the determination of vanadium by titration with potassic hypermanganate the following points require attention.

For the reduction of vanadic pentoxide to dioxide, it is best, after adding dilute sulphuric acid, to boil with a solution of sulphurous acid and afterward to evaporate the solution nearly, at least, to dryness upon a water bath, so as to insure a perfect reduction and at the same time to expel the last traces of sulphurous oxide. Sulphydric acid gas also readily reduces the vanadic pentoxide in presence of sulphuric acid, but there is almost always a separation of free sulphur in a state of extreme subdivision. This passes readily through the filter, and the results of the titration are not so satisfactory as when sulphurous acid is employed as the reducing agent. The solution of vanadic dioxide should be diluted till the color is pale blue, heated to about  $80^{\circ}$ – $100^{\circ}$ , and titrated hot. In the hot solution the disappearance of the hypermanganate takes place instantly, and the end reaction is much more quickly and satisfactorily attained. The actual results are precisely the same as when a cold solution is employed, as the following titrations sufficiently prove.

- I. In a cold solution of  $\text{VO}_2$  in  $\text{SO}_4\text{H}_2$  three successive portions of 200 cc. each required 4.62 cc., 4.64 cc., and 4.63 cc. of hypermanganate solution.
- II. At  $53^\circ \text{C}$ . 200 cc. as before required 4.62 cc.
- III. At  $62^\circ \text{C}$ . 200 cc. required 4.66 cc. Process rather more rapid.
- IV. At  $70^\circ \text{C}$ . " " 4.66 cc. " " "
- V. At  $80^\circ \text{C}$ . " " 4.65 cc. Color vanished instantly.
- VI. At  $100^\circ \text{C}$ . " " 4.64 cc. " " "

The following analyses will show the effect of reducing by hydric sulphide, as compared with reduction by sulphurous acid. In an acid sodic vanadate: —

- I. 0.0908 gr. gave 0.0406 gr.  $\text{V}_2\text{O}_5 = 44.67\%$  with  $\text{H}_2\text{S}$
- II. 0.1381 gr. " 0.0607 gr. " = 43.92% "
- III. 0.1540 gr. " 0.0692 gr. " = 44.90% "
- IV. 0.1625 gr. " 0.0696 gr. " = 42.99% with  $\text{SO}_2\text{H}_2$
- V. 0.1532 gr. " 0.0659 gr. " = 43.01% "

When hydric sulphide is used as a reducing agent, it often happens that the filtrate on evaporation deposits more sulphur. In titrating with hypermanganate, the final color reaction must be permanent for ten to fifteen minutes at least. As usual, the amount of hypermanganate required to color an equal volume of water and dilute sulphuric acid must be determined, and the proper correction applied.

In my paper on the vanadio-molybdates I have given another method of determining vanadium based upon the fact that a ferrous salt readily reduces vanadic pentoxide in the presence of free chlorhydric acid. I have since found that this method is not new, but was proposed and tested by Otto Lindemann \* some years since.

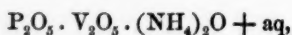
**1 : 1 Ammonic Phospho-vanadate.** — When any ammonic vanadate is dissolved with an excess of ammonic phosphate, and nitric acid is cautiously added in small quantities at a time, a deep orange-red solution is obtained, which on heating becomes colorless, but which on evaporation to a small volume yields beautiful bright yellow granular crystals. These are to be carefully washed with cold water, in which they are not very soluble. The solution has at first a fine yellow color, but on continued dilution with water passes through the changes in color which have already been described. In this salt,

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\* Ueber die quantitative Bestimmung des Vanadins. Inaugural Dissertation von Otto Lindemann. Jena, 1879.

0.5582 gr. lost on ignition with $\text{WO}_4\text{Na}_2$	0.1017 gr. = 18.22%
0.7667 gr. " " "	0.1393 gr. = 18.17%
0.5329 gr. gave 0.0707 gr. $(\text{NH}_4)_2\text{O}$	= 13.28%
0.9753 gr. " 0.4501 gr. $\text{V}_2\text{O}_5$ with $\text{KMnO}_4$	= 46.15%
0.6883 gr. " 0.3174 gr. " "	= 46.13%
0.1073 gr. " 0.0495 gr. " "	= 46.15%

The analyses lead to the formula



which requires :

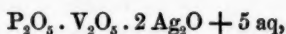
		Calc'd.	Mean.
$\text{P}_2\text{O}_5$	142	35.99	35.67
$\text{V}_2\text{O}_5$	182.6	46.27	46.14
$(\text{NH}_4)_2\text{O}$	52	13.17	13.28
$\text{H}_2\text{O}$	18	4.57	4.91
	<hr/> 394.6	<hr/> 100.00	

I have here assumed that the simplest expression of the results of the analyses represents the molecular weight. It will, I think, appear from the study of other compounds, that it is at least probable that the molecular weight is much higher. The solution of the salt is very easily reduced by dust or traces of organic matter. The solution then contains a greater or less proportion of a phospho-vanadico-vanadate. The solution of the salt has a yellow color and a very strong acid reaction, but this probably depends simply upon the decomposition which sets phosphoric acid free.

**1 : 1 Argentic Phospho-vanadate.** — A quantity of the above-described ammonium salt was dissolved with ammoniac phosphate, and argentic nitrate added to the solution in excess. A sulphur-yellow crystalline precipitate was at once formed, which was digested with very dilute nitric acid so as to remove argentic phosphate, and then presented granular yellow crystals but slightly soluble in cold or hot water. The salt is readily decomposed by dilute chlorhydric acid, and then yields a yellow solution which is probably the acid of the series. In the silver salt,

1.4134 gr. gave 0.9192 gr. $\text{AgCl}$	= 52.59% $\text{Ag}_2\text{O}$
1.6267 gr. " 0.7938 gr. metallic silver	= 52.41% "
1.3696 gr. " 0.2851 gr. $\text{V}_2\text{O}_5$	= 20.82%
0.10193 gr. lost on ignition 0.1067 gr.	= 10.47%

The analyses lead to the formula



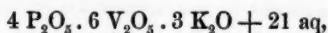
which requires :

		Calc'd.	Found.	
$\text{P}_2\text{O}_5$	142	16.19	16.21	
$\text{V}_2\text{O}_5$	182.6	20.83	20.82	
$2 \text{Ag}_2\text{O}$	464	52.70	52.59	52.41
$5 \text{H}_2\text{O}$	90	10.28	10.47	
	<u>478.6</u>	<u>100.00</u>		

6 : 4 *Potassic Phospho-vanadate*. — When ammonio-magnesian phosphate,  $\text{P}_2\text{O}_5 \cdot \text{Mg}_2(\text{NH}_4)_2$ , is boiled with a strong solution of potassic divanadate, the phosphate disappears and is replaced by yellow granular masses, which are but slightly soluble in water. In this salt, after washing with cold water,

0.5401 gr. gave 0.3852 gr.  $\text{P}_2\text{O}_5$  and  $\text{V}_2\text{O}_5$  = 71.31 %  
 { 0.3790 gr. " 0.1777 gr.  $\text{V}_2\text{O}_5$  with  $\text{KMnO}_4$  = 46.89 %  
 { 0.3790 gr. lost on ignition (alone) 0.0619 gr. = 16.31 %

The analyses lead to the formula



which requires :

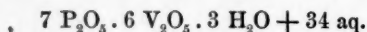
		Calc'd.	Found.	
$4 \text{P}_2\text{O}_5$	568	24.41	24.42	71.31
$6 \text{V}_2\text{O}_5$	1098	47.18	46.89	
$3 \text{K}_2\text{O}$	283	12.16	12.38	28.69
$21 \text{H}_2\text{O}$	378	16.25	16.31	
	<u>2327</u>	<u>100.00</u>		

No magnesium and no ammonium could be detected in the salt, and it seems at least probable that the salts of the series might be prepared by the same process, other acid vanadates being substituted for the potassic salt employed. A strong solution in cold water gave a brick-red fine granular precipitate with argentic nitrate, and yellow flocky precipitates with mercurous and thalious nitrates. The mercurous precipitate was distinctly seen to contain two different compounds, and it is therefore probable that the potassic salt was decomposed even by a small quantity of cold water.

7 : 6 *Hydric Phospho-vanadate*. — When a solution of phosphoric acid is mixed with a strong solution of sodic divanadate, a yellow uncrystalline mass is formed. This after standing some days becomes distinctly crystalline, and may be washed with cold water until the washings become orange-red. In a preparation of this salt, dried as usual upon woollen paper,

1.2172 gr. gave 0.4846 gr.  $V_2O_5$  = 39.81%  
 0.8553 gr. " 0.6487 gr. mixed oxides = 75.84%  $P_2O_5 + V_2O_5$   
 0.6127 gr. lost with  $WO_4Na_2$  0.1470 gr. = 24.00% water.

The analyses show that the compound analyzed contained no soda, and that it is a 7 : 6 phospho-vanadic acid, the formula of which may be written



The formula requires :

		Calc'd.		Found.	
7 $P_2O_5$	994	39.76	} 75.83	39.81	} 75.84
6 $V_2O_5$	1096	36.07		36.03	
37 $H_2O$	666	24.17		24.00	
	<hr/> 2756	<hr/> 100.00			

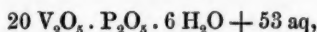
The sum of the phosphoric and vanadic oxides found by difference is 76.00. After all saline matters are washed out, the acid dissolves readily in water, and gives an orange solution, which changes color on dilution in the manner already explained. I shall, after describing the phospho-vanadico-vanadates and arsenio-vanadico-vanadates, return to this and the preceding compounds.

20 : 1 *Phospho-vanadic Acid*. — When a solution of phosphoric acid is mixed with one of ammonic metavanadate, the liquid becomes orange, but after heating for a time upon a water-bath lemon-yellow, and then deposits a large quantity of a lemon-yellow crystalline salt. More of this salt is deposited on evaporating the mother liquor, and again after partially neutralizing with ammonia. The yellow salt may be drained with the filter-pump and then washed with a small quantity of cold water. The salt presents fine yellow crystals which dissolve in a small quantity of hot water. The liquid is at first yellow, but on adding more hot water, and especially on heating, it becomes orange; with more water, orange-red, and finally deep garnet-red with a very strong acid reaction. If this solution is evaporated upon a water-bath the changes of color occur in the inverse order; that is to say, the liquid

gradually becomes orange-red, orange, and yellow, and the original salt is finally deposited. The changes of color observed are due to the decomposition of the ammonium salt by water, and the formation of ammonic phosphates and of phospho-vanadates differing in constitution from the original compound and containing a greater proportion of vanadic pentoxide for one molecule of phosphoric oxide. Phosphoric acid is also set free in the reaction. The deep red solution, on standing, deposits beautiful small granular ruby or garnet-red crystals. Of these crystals,

$$\begin{cases} 0.3156 \text{ gr. lost on ignition (alone)} & 0.0691 \text{ gr.} = 21.89\% \\ 0.3156 \text{ gr. gave with KMnO}_4 & 0.2377 \text{ gr.} = 75.32\% \end{cases}$$

The analyses correspond with the formula



which requires :

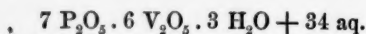
		Calc'd.	Found.
20 V <sub>2</sub> O <sub>5</sub>	3660	75.24	75.32
P <sub>2</sub> O <sub>5</sub>	142	2.92	2.79
59 H <sub>2</sub> O	1062	21.84	21.89
	4864	100.00	

The phosphoric oxide was determined by the difference. The solution of the acid has a dark red color and a strongly acid reaction. It gives cinnamon-colored flocky precipitates with nitrates of silver and thallium. The silver salt is readily decomposed by potassic chloride in presence of a trace of chlorhydric acid, giving a red solution which deposits beautiful square thin tabular crystals, the red color of which is so deep that they appear black by reflected light. In preparing the salts of this series it will probably be best to saturate a small proportion of the acid with an alkaline base, and then to add the rest of the acid. For the present the basicity of the acid is undetermined, and the assumption that it contains six molecules of water is merely provisional. It also appears probable that salts of this and similar higher series may be prepared by mixing solutions of alkaline metavanadates with those of alkaline phosphates in definite proportions, and then adding dilute sulphuric acid in small portions at a time, stirring or shaking after each addition of acid. The precise quantity of acid to be added should be calculated beforehand, which may of course be easily done if we assume a definite basicity, as, for instance, that each molecule of salt shall contain three molecules of fixed base.

**7 : 6 Hydric Phospho-vanadate.** — When a solution of phosphoric acid is mixed with a strong solution of sodic divanadate, a yellow uncrystalline mass is formed. This after standing some days becomes distinctly crystalline, and may be washed with cold water until the washings become orange-red. In a preparation of this salt, dried as usual upon woollen paper,

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 0.6127 gr. lost with  $WO_4Na_2$  0.1470 gr. = 24.00% water.

The analyses show that the compound analyzed contained no soda, and that it is a 7 : 6 phospho-vanadic acid, the formula of which may be written



The formula requires :

		Calc'd.		Found.	
7 $P_2O_5$	994	39.76	} 75.83	39.81	} 75.84
6 $V_2O_5$	1096	36.07		36.03	
37 $H_2O$	666	24.17		24.00	
	<hr/> 2756	<hr/> 100.00			

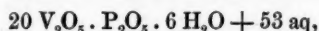
The sum of the phosphoric and vanadic oxides found by difference is 76.00. After all saline matters are washed out, the acid dissolves readily in water, and gives an orange solution, which changes color on dilution in the manner already explained. I shall, after describing the phospho-vanadico-vanadates and arsenio-vanadico-vanadates, return to this and the preceding compounds.

**20 : 1 Phospho-vanadic Acid.** — When a solution of phosphoric acid is mixed with one of ammonic metavanadate, the liquid becomes orange, but after heating for a time upon a water-bath lemon-yellow, and then deposits a large quantity of a lemon-yellow crystalline salt. More of this salt is deposited on evaporating the mother liquor, and again after partially neutralizing with ammonia. The yellow salt may be drained with the filter-pump and then washed with a small quantity of cold water. The salt presents fine yellow crystals which dissolve in a small quantity of hot water. The liquid is at first yellow, but on adding more hot water, and especially on heating, it becomes orange; with more water, orange-red, and finally deep garnet-red with a very strong acid reaction. If this solution is evaporated upon a water-bath the changes of color occur in the inverse order; that is to say, the liquid

gradually becomes orange-red, orange, and yellow, and the original salt is finally deposited. The changes of color observed are due to the decomposition of the ammonium salt by water, and the formation of ammoniac phosphates and of phospho-vanadates differing in constitution from the original compound and containing a greater proportion of vanadic pentoxide for one molecule of phosphoric oxide. Phosphoric acid is also set free in the reaction. The deep red solution, on standing, deposits beautiful small granular ruby or garnet-red crystals. Of these crystals,

$$\begin{cases} 0.3156 \text{ gr. lost on ignition (alone)} & 0.0691 \text{ gr.} = 21.89\% \\ 0.3156 \text{ gr. gave with } \text{KMnO}_4 & 0.2377 \text{ gr.} = 75.32\% \end{cases}$$

The analyses correspond with the formula



which requires :

		Calc'd.	Found.
20 $\text{V}_2\text{O}_5$	3660	75.24	75.32
$\text{P}_2\text{O}_5$	142	2.92	2.79
59 $\text{H}_2\text{O}$	1062	21.84	21.89
	<hr/> 4864	<hr/> 100.00	

The phosphoric oxide was determined by the difference. The solution of the acid has a dark red color and a strongly acid reaction. It gives cinnamon-colored flocky precipitates with nitrates of silver and thallium. The silver salt is readily decomposed by potassic chloride in presence of a trace of chlorhydric acid, giving a red solution which deposits beautiful square thin tabular crystals, the red color of which is so deep that they appear black by reflected light. In preparing the salts of this series it will probably be best to saturate a small proportion of the acid with an alkaline base, and then to add the rest of the acid. For the present the basicity of the acid is undetermined, and the assumption that it contains six molecules of water is merely provisional. It also appears probable that salts of this and similar higher series may be prepared by mixing solutions of alkaline metavanadates with those of alkaline phosphates in definite proportions, and then adding dilute sulphuric acid in small portions at a time, stirring or shaking after each addition of acid. The precise quantity of acid to be added should be calculated beforehand, which may of course be easily done if we assume a definite basicity, as, for instance, that each molecule of salt shall contain three molecules of fixed base.

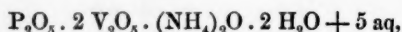
## PHOSPHO-DIVANADATES.

The salts of this series are formed under conditions which have already been pointed out. They have frequently, at least, a fine yellow color, and are decomposed by water with formation of salts of other series.

*Phospho-divanadate of Ammonium.* — This is the yellow crystalline salt referred to as formed by the action of phosphoric acid upon ammonic metavanadate. The salt dissolves in a small quantity of cold water without apparent decomposition, but the reactions of the solution are at best rather uncertain. Argentic nitrate gives a fine bright yellow crystalline precipitate. In the ammonium salt,

1.1259 gr. lost on ignition 0.2876 gr. = 25.54%  $\text{NH}_3$  and  $\text{H}_2\text{O}$   
 1.0600 gr. " " with  $\text{WO}_3\text{Na}_2$  0.2723 gr. = 25.69%  
 1.0624 gr. gave 0.1676 gr.  $\text{NH}_4\text{Cl}$  = 7.67%  $(\text{NH}_4)_2\text{O}$   
 1.4112 gr. " 0.7534 gr.  $\text{V}_2\text{O}_5$  = 53.40%

The analyses lead to the formula



which requires :

		Calc'd.	Found.
$\text{P}_2\text{O}_5$	142	20.74	20.98 (diff.)
$2 \text{V}_2\text{O}_5$	365	53.28	53.40
$(\text{NH}_4)_2\text{O}$	52	7.59	7.67
$7 \text{H}_2\text{O}$	126	18.39	17.95
	<hr/> 685	<hr/> 100.00	

The formula given corresponds to the provisional assumption of three molecules of water in the acid.

## ARSENIO-VANADATES.

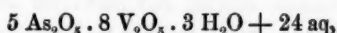
These salts are formed under precisely the same conditions as those which determine the formation of phospho-vanadates. The general characters of the salts are almost precisely similar. Like the phosphorus compounds, they are yellow or orange-yellow and crystalline. They are decomposed by water, and yield deep orange-red salts of new series, in which the proportion of vanadic to phosphoric oxide is largely increased.

*Analytical Methods.* — Arsenic is most conveniently determined in these salts by reduction with sulphurous acid and precipitation of arsenious sulphide by sulphydric acid. The sulphide is then to be weighed upon an asbestos filter. In the filtrate which contains the vanadium as dioxide the vanadic pentoxide may be determined by potassic hypermanganate. Dilute sulphuric acid is to be added in place of chlorhydric acid before precipitation with sulphydric acid. Water cannot be accurately determined in these salts by ignition with sodic tungstate, as a greater or less quantity of arsenic oxide is always volatilized. The best method consists in cautiously heating the salt over a radiating cup of sheet-iron until a constant weight is obtained.

*5 : 8 Arsenio-vanadic Acid.* — When sodic divanadate and arsenate are dissolved together in boiling water, and nitric acid is added in small portions at a time, a deep orange liquid is obtained which on evaporation to dryness upon a water-bath yields an orange-yellow crystalline mass. This is to be purified by careful washing with cold water, when a beautiful crystalline orange-colored salt remains. The salt is somewhat soluble in cold, and readily in hot water. The solution is very easily reduced by dust or other organic matters, and becomes greenish-orange with formation of a greater or less quantity of an arsenio-vanadico-vanadate. It is then difficult to reoxidize the solution so as to obtain the original compound. On analysis,

{ 0.8558 gr. gave 0.3374 gr. $\text{As}_2\text{S}_3$	= 36.87% $\text{As}_2\text{O}_3$
{ 0.8558 gr. " 0.4058 gr. $\text{V}_2\text{O}_5$ with $\text{KMnO}_4$	= 47.41%
0.8715 gr. lost over a radiator 0.1358 gr.	= 15.58%

The analyses correspond to the formula



which requires :

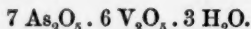
		Calc'd.		Found.
5 $\text{As}_2\text{O}_3$	1150	47.18	} 84.31	47.41
8 $\text{V}_2\text{O}_5$	1461	37.13		36.87
27 $\text{H}_2\text{O}$	486	15.69		15.58
	3097	100.00		99.86

The water, as estimated by difference, amounts to 15.72, so that the direct determination is nearly correct, and no fixed base is present. In a second preparation, in which I employed residues containing arsenic and vanadium from the preparation of the arsenio-vanadico-vanadates

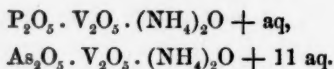
to be described and oxidized with nitric acid and potassic hypermanganate, I found the ratio of the arsenic to the vanadic oxide to be as 7 : 6.

$$\begin{cases} 1.2105 \text{ gr. gave } 0.5825 \text{ gr. As}_2\text{S}_3 = 44.99\% \text{ As}_2\text{O}_3 \\ 1.2105 \text{ gr. " } 0.3748 \text{ gr. V}_2\text{O}_5 = 30.97\% \end{cases}$$

The difference here cannot be taken as water, as some manganous oxide was present; but the acid may, like the corresponding phosphorus compound, be regarded as



Since the publication of the preliminary notice in which I announced the discovery of this class of compounds,\* and threw the whole subject open to chemists, a short paper has appeared by F. Fernandez,† in which the writer describes an arsenio-vanadate of ammonium, which, except so far as water of crystallization is concerned, corresponds to the ammonic phospho-vanadate which I have described, so that we now have



Want of material has prevented a more complete study of the subject on my own part.

#### PHOSPHO-VANADICO-VANADATES.

The salts of this series are very readily formed by boiling an excess of a mixture of vanadic dioxide and pentoxide with alkaline phosphates, when the mixed oxides dissolve to form red or greenish-red solutions, which on cooling yield in many instances very beautiful crystalline salts. The same result is obtained by fusing the mixture of oxides obtained by igniting ammonic metavanadate with alkaline phosphates; by partially reducing phospho-vanadates, or by adding solutions of vanadic dioxide to solutions of phospho-vanadates. The alkaline phospho-vanadico-vanadates are often very beautiful, and present extremely well-defined crystals. They have usually a green color, which may be so deep as to appear black in large crystals. By oxidation they pass into phospho-vanadates.

\* American Chemical Journal, iv. 577.

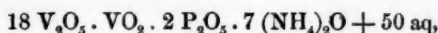
† Berichte der Deutschen Chem. Gesellschaft, xvii. 1632. July, 1884.

*Analytical Methods.* — These are the same as those described for the analysis of phospho-vanadates. The vanadic dioxide may be determined directly by titration with potassic hypermanganate in dilute solutions containing free sulphuric acid. In another portion of the solutions the vanadic pentoxide is to be reduced with sulphurous acid, and then determined by titration. The whole quantity of oxides may be found by mercurous nitrate and mercuric oxide after completely oxidizing the vanadic dioxide with nitric acid.

18 : 1 : 2 *Phospho-vanadico-vanadates of Ammonium.* — When a solution of phospho-vanadate of ammonium is mixed with one of vanadic dioxide in chlorhydric acid, and the liquid is allowed to stand for some time, beautiful deep green prismatic crystals are deposited. These dissolve in hot water to a very deep red solution, and appear to be decomposed exactly in the manner which has been explained in the case of the phospho-vanadates. Of this salt,

0.3647 gr. lost on ignition with $\text{WO}_3\text{Na}_2$	0.0938 gr.	= 25.72%
0.5318 gr. gave 0.3657 gr. $\text{V}_2\text{O}_5$ and $\text{P}_2\text{O}_5$		= 68.76%
{ 0.4958 gr. " 0.0084 gr. $\text{VO}_2$ with $\text{KMnO}_4$		= 1.68%
{ 0.4958 gr. " 0.0083 gr. $\text{VO}_2$ with iodine and $\text{CO}_2\text{NaH}$		= 1.69%
0.4284 gr. " 0.0325 gr. $(\text{NH}_4)_2\text{O}$		= 7.59%

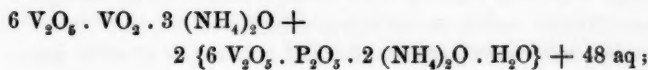
The vanadic dioxide was oxidized with nitric acid before precipitation with mercurous nitrate and mercuric oxide. The resulting percentage is to be corrected accordingly. The analyses correspond fairly well with the formula



which requires :

		Calc'd	Found.	
18 $\text{V}_2\text{O}_5$	3294	66.88	67.08	
$\text{VO}_2$	83	1.69	1.68	1.74
2 $\text{P}_2\text{O}_5$	284	5.77	5.51	
7 $(\text{NH}_4)_2\text{O}$	364	7.39	7.59	
50 $\text{H}_2\text{O}$	900	18.27	18.13	
	4925	100.00		

The phosphoric oxide is determined by difference only. The compound may also be regarded as a double salt ; as, for instance,



but we have at present no data for deciding the question. The solution in cold water gives brown flocky precipitates with salts of silver and thallium and with mercurous nitrate, none with baric chloride at first, but after a short time the mixture becomes turbid and then deposits distinct orange crystals mixed with a brown flocky matter. The salt is therefore probably decomposed by solution.

4 : 5 : 1 *Phospho-vanadico-vanadate of Sodium*. — A boiling solution of sodic orthophosphate dissolves the mixture of vanadic oxides obtained by igniting ammoniac metavanadate, and gives a greenish liquid which on cooling deposits green crystalline scales with a talcose lustre. The same salt is formed by fusing together the mixed oxides and sodic phosphate, but is in this way more difficult to obtain in a state of purity. The compound is insoluble in water, and cannot therefore be purified by recrystallization. Of this salt,

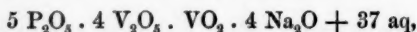
1.4264 gr. lost on ignition 0.3904 gr. = 27.37% water

1.2893 gr. gave 0.8136 gr.  $V_2O_5 + P_2O_5 = 63.10\%$

1.7149 gr. " 0.5815 gr.  $V_2O_5$  by titration with  $KMnO_4 = 33.90\%$

1.4190 gr. " 33.67% and 33.75%

The analyses correspond tolerably well with the formula



which requires :

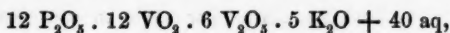
		Calc'd.	Found.	
5 $P_2O_5$	710	29.11	29.15	29.32 (diff.)
4 $V_2O_5$	732	30.01	30.66	
$VO_2$	83	3.40	3.11	
4 $Na_2O$	248	10.17	9.74	
37 $H_2O$	666	27.31	27.17	
	<hr/> 2439	<hr/> 100.00		

12 : 12 : 6 *Potassic Phospho-vanadico-vanadate*. — When solutions of potassic divanadate and potassic orthophosphate,  $PO_4K_2H$ , are heated together, the phosphate being in large excess, a colorless solution is formed. A solution of vanadic dioxide in a large excess of chlorhydric acid then often produces almost immediately a precipitate of black granular crystals. In some cases, however, the black salt is formed only after standing some hours. Under the microscope the black crystals appear to be cubes, though this is rather uncertain. The true color is deep green. The salt is insoluble in water contain-

ing other saline bodies; but as soon as the crystals are completely washed, they dissolve readily in hot water with decomposition, a beautiful green salt crystallizing from the solution on standing. Of the black crystals,

0.4978 gr. lost with $\text{WO}_4\text{Na}_2$	0.0716 gr.	= 14.38 $\text{H}_2\text{O}$
0.1622 gr. gave with $\text{KMnO}_4$	0.03177 gr. $\text{VO}_2$	= 19.59%
0.1201 gr. " "	0.02384 gr. " "	= 19.84%
0.1383 gr. " "	0.06032 gr. $\text{V}_2\text{O}_5$	= 43.62%
0.1360 gr. " "	0.05892 gr. " "	= 43.32%
0.5646 gr. gave	0.3035 gr. $\text{P}_2\text{O}_5$	= 34.38% $\text{P}_2\text{O}_5$
0.7186 gr. " "	0.3876 gr. " "	= 34.49% " "

The analyses lead to the formula



which requires :

		Calc'd.	Found.	
12 $\text{P}_2\text{O}_5$	1704	34.14	34.38	34.49
12 $\text{VO}_2$	999	20.02	19.84	19.59
6 $\text{V}_2\text{O}_5$	1096	21.96	22.02	22.72
5 $\text{K}_2\text{O}$	472	9.46	9.11	
40 $\text{H}_2\text{O}$	720	14.42	14.38	
	4991	100.00		

The sum of the three oxides  $\text{P}_2\text{O}_5 + \text{VO}_2 + \text{V}_2\text{O}_5 = 76.12$ , as calculated from the formula, and 76.51 as found from the mean of all the analyses. The analyses are very difficult, partly because no perfectly satisfactory method of separating phosphoric oxide from the other oxides has yet been found, and partly because in titrating vanadic dioxide by potassic hypermanganate the end reaction varies with the quantity of phosphoric oxide present. It is true that this variation is usually within narrow limits, but it is sometimes sufficient to affect the result by as much as 0.50%.

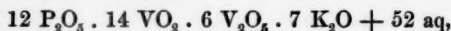
The beautiful crystalline green salt which is formed when the black salt above described is dissolved in hot water was also analyzed.

0.5918 gr. gave	0.3771 gr. $\text{PtCl}_6\text{K}_2$	= 12.37% $\text{K}_2\text{O}$
0.4766 gr. lost with $\text{WO}_4\text{Na}_2$	0.0718 gr.	= 15.06%
0.1617 gr. gave with $\text{KMnO}_4$	0.03405 gr. $\text{VO}_2$	= 21.06%
0.1274 gr. " "	0.02708 gr. " "	= 21.26%

0.0840 gr. gave with $\text{KMnO}_4$	0.01778 gr. $\text{VO}_2$	= 21.16%
0.1532 gr. " "	0.0659 gr. $\text{V}_2\text{O}_5$	= 43.01%
0.1612 gr. " "	0.0689 gr. " "	= 42.77%
0.1625 gr. " "	0.0699 gr. " "	= 42.99%

In the determination of the water by fusion with sodic tungstate, the vanadic dioxide is oxidized to pentoxide. Hence it is necessary to add to the percentage of water found — 15.06 — the percentage of oxygen required to convert 21.16% (mean) of  $\text{VO}_2$  to the equivalent quantity of  $\text{V}_2\text{O}_5$  or 2.03%. This correction was not applied in the case of the first salt described above, because after a rapid fusion the vanadic dioxide appeared not to have been oxidized. In determining the vanadic pentoxide in these salts the oxide is first reduced to  $\text{VO}_2$  by boiling with sulphurous acid and then titrated with hypermanganate. From want of material the phosphoric oxide in the green salt was determined by difference only.

The analyses of the green salt correspond with the formula



which requires:

		Calc'd.	Mean.			
12 $\text{P}_2\text{O}_5$	1704	30.63	29.65 (diff.)			
14 $\text{VO}_2$	1166	20.96	21.16	21.06	21.26	21.16
6 $\text{V}_2\text{O}_5$	1096	19.71	19.73	19.82	19.80	19.58
7 $\text{K}_2\text{O}$	661	11.88	12.37		12.37	
52 $\text{H}_2\text{O}$	936	16.82	17.09		17.09	
	5563	100.00				

In this class of compounds I found it impossible to determine the sum of the acid-forming oxides by precipitating directly with mercurous nitrate and mercuric oxide. The results of many trials varied within very wide limits. Both the black and green salts are oxidized when heated with nitric acid and evaporated to degrees. Yellow crystalline masses remain, which contain phospho-vanadates, and which deserve a careful study as furnishing a new and perhaps better mode of forming that class of salts.

14 : 16 : 6 *Ammonic Phospho-vanadico-vanadate*. — When ammoniac metavanadate or divanadate is boiled with a solution of ammoniac orthophosphate in large excess, a colorless liquid is formed, which gives, with a solution of vanadic dioxide in chlorhydric acid, after a time, beautiful black or rather intensely deep green crystals, exactly resembling those of the potassic salt already described. The crystals

dissolve easily in hot water free from saline matter, but do not crystallize readily from the solution. Of this salt, after careful washing and drying only,

0.7744 gr. lost with  $\text{WO}_4\text{Na}_2$  0.1859 gr. = 24.01%  $\text{NH}_3 + \text{H}_2\text{O}$ . The oxygen gained by the vanadic dioxide is 2.14% and  $24.01 + 2.14 = 26.15\%$   $\text{NH}_3 + \text{H}_2\text{O}$

0.5556 gr. gave when heated in a combustion tube 0.1451 gr. = 26.11%  $\text{NH}_3 + \text{H}_2\text{O}$

0.8969 gr. gave with  $\text{KMnO}_4$  0.2001 gr.  $\text{VO}_2 = 22.31\%$

0.2018 gr. " " 0.0444 gr. " = 22.19%

0.5626 gr. after reduction with  $\text{SO}_3\text{H}_2$  gave with  $\text{KMnO}_4$  0.2427 gr. = 43.13%  $\text{V}_2\text{O}_5$

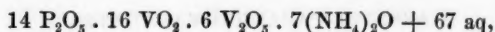
0.2494 gr. after reduction with  $\text{SO}_3\text{H}_2$  gave with  $\text{KMnO}_4$  0.1067 gr. = 42.76%  $\text{V}_2\text{O}_5$

0.5325 gr. gave 0.0326 gr.  $(\text{NH}_4)_2\text{O} = 6.13\%$

0.5053 gr. " 0.0309 gr. " = 6.12%

The mean of the two determinations of  $\text{VO}_2$  is 22.25%, and the equivalent in  $\text{V}_2\text{O}_5$  24.38%, which, subtracted from 42.76 and 43.13 respectively gives 18.38 and 18.75 for the percentages of  $\text{V}_2\text{O}_5$ .

The analyses correspond closely with the formula



which requires:

		Calc'd.	Found.	
14 $\text{P}_2\text{O}_5$	1988	33.21	33.06 (diff.)	
16 $\text{VO}_2$	1333	22.26	22.31	22.19
6 $\text{V}_2\text{O}_5$	1096	18.30	18.38	18.75
7 $(\text{NH}_4)_2\text{O}$	364	6.08	6.12	6.13
67 $\text{H}_2\text{O}$	1206	20.15	20.01	
	5987	100.00		

A portion of the very dark green salt was boiled with water, and the deep green solution allowed to stand, when much lighter green crystals separated. These were again dissolved and recrystallized. The crystals had a peculiar rusty olive-green surface color. Of this salt,

0.4770 gr. gave 0.1013 gr.  $\text{V}_2\text{O}_5$  by  $\text{KMnO}_4 = 21.21\%$  and

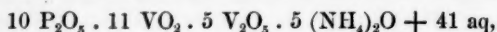
0.1014 gr.  $\text{VO}_2 = 21.22\%$

0.4014 gr. gave 0.0249 gr.  $(\text{NH}_4)_2\text{O} = 6.20\%$

0.3062 gr. lost with  $\text{WO}_4\text{Na}_2$  0.0663 gr. = 21.65%

The determination of the sum of the water and ammonia must in this case be corrected for the oxygen required to convert the 21.22% of vanadic dioxide into vanadic pentoxide, since the ignition was continued with free access of air until the weight of the mass became constant. The correction is of course to be added, so that we have for the total loss  $21.65 + 2.03 = 23.68\%$ .

The analyses correspond tolerably well only with the formula



which requires :

		Calc'd.	Found.
10 $\text{P}_2\text{O}_5$	1420	33.44	33.89
11 $\text{VO}_2$	916	21.57	21.21
5 $\text{V}_2\text{O}_5$	913	21.49	21.22
5 $(\text{NH}_4)_2\text{O}$	260	6.12	6.20
41 $\text{H}_2\text{O}$	738	17.38	17.48
	<u>4247</u>	<u>100.00</u>	

As the number of molecules of vanadic dioxide in this salt is uneven, it will be necessary to double the formula in order to obtain a symmetrical structural scheme.

#### ARSENIO-VANADICO-VANADATES.

The salts of this series are formed with great ease by mixing solutions of alkaline arsenates and vanadates, and adding a solution of vanadic dioxide in excess of chlorhydric acid. On evaporation large very dark green crystals are deposited in abundance. In preparing arsenio-vanadates it is difficult to avoid a partial reduction of the vanadic pentoxide by dust or other organic matter, and as a rule solutions are obtained which contain both classes of salts. The arsenio-vanadico-vanadates form a very beautiful and well-defined class of salts.

*Analytical Methods.* — Vanadic dioxide may be determined directly by titration with hypermanganate after addition of sulphuric acid and appropriate dilution. To determine the arsenic present as arsenic pentoxide, the arsenic is first to be brought into the form of arsenous oxide by means of sulphurous acid after adding a little sulphuric acid to the solution. The arsenic may then be precipitated as sulphide by means of sulphhydric acid, and weighed on a Gooch filter. The filtrate contains all the vanadium in the form of dioxide, which may then be determined by means of hypermanganate. The relation between the two oxides of vanadium is then easily found. The accurate determination

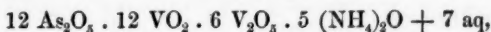
of the water of crystallization in these salts is difficult. They all lose arsenic oxide when heated with sodic tungstate, and the only method which can be safely employed consists in heating weighed portions over a radiating cup of sheet-iron until a constant weight is obtained.

**12:12:6 Ammonium Salt.** — When ammonic metavanadate or divanadate is boiled with a large excess of ammonic arsenate, a colorless solution is formed. On adding a solution of vanadic dioxide in chlorhydric acid, a dark blue precipitate is formed, which dissolves readily in an excess of dilute chlorhydric acid. No precipitate is formed if the solution of the dioxide contains enough free acid. After standing some hours, a very dark green, almost black, crystalline salt is deposited in quantity. This is to be washed with cold water. The crystals exactly resemble those of the black potassic phospho-vanadico-vanadate already described. They are insoluble in saline solutions, and but slightly soluble in cold water. The solution has a greenish-yellow color. It gives a brick-red indistinctly crystalline precipitate with argentic nitrate, and a dull yellow flocky precipitate with mercurous nitrate. This last becomes crystalline on standing. It will serve to prepare other salts of this series by double decomposition with chlorides. The solution of the salt gives no precipitate with cupric sulphate or baric chloride. In this salt,

1.1623 gr. gave with $\text{KMnO}_4$	0.2199 gr. $\text{VO}_2$	= 18.91%
0.8719 gr. " "	0.3605 gr. $\text{V}_2\text{O}_5$	= 41.37%
0.9726 gr. gave	0.5500 gr. $\text{As}_2\text{S}_3$	= 52.87%
0.8246 gr. " "	0.4646 gr. "	= 52.68%
1.0209 gr. " "	0.0538 gr. $(\text{NH}_4)_2\text{O}$	= 5.27%

The vanadic pentoxide, after deducting the equivalent of the dioxide found, is 20.65%. The water could not be determined either by heating with sodic tungstate or in a combustion tube, as arsenous oxide sublimed in each case. It is therefore estimated by difference.

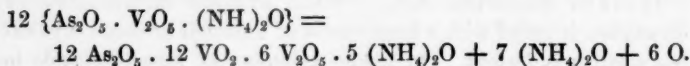
The analyses agree fairly well with the formula



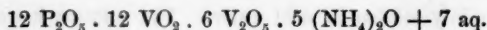
which requires:

		Calc'd.	Found.	
12 $\text{As}_2\text{O}_5$	2760	52.65	52.68	52.87
12 $\text{VO}_2$	1000	19.08	18.91	
6 $\text{V}_2\text{O}_5$	1096	20.91	20.65	
5 $(\text{NH}_4)_2\text{O}$	260	4.96	5.27	
7 $\text{H}_2\text{O}$	126	2.40	2.40	
	5242	100.00		

It will be observed that this salt may be considered as derived from twelve molecules of an arsenio-vanadate by reduction of one half the vanadic pentoxide to dioxide and loss of seven molecules of ammoniac oxide, since we have



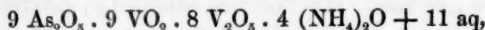
This relation might be made available in the preparation of the salt. Boiling water instantly decomposes this compound, and gives a deep green solution, which on standing deposits crystals of a peculiar deep olive-green color with a tinge of brown. The black salt corresponds exactly in composition to a phosphorus compound above described, except only as regards water of crystallization:



9:9:8 *Ammonium-salt*. — When boiling water is poured upon the black salt, it instantly becomes deep olive-green upon the surface, and then dissolves to a deep green liquid, which on cooling deposits crystals with a dull olive-green surface color. These may be redissolved and recrystallized a second time. The mother liquor from these crystals has a bright green color, and contains much vanadic acid. In the olive-green salt,

0.4061 gr. gave 0.0167 gr. $(\text{NH}_4)_2\text{O}$	= 4.12%
{ 0.2871 gr. " 0.1370 gr. $\text{As}_2\text{S}_3$	= 44.61%
{ 0.2871 gr. " 0.1393 gr. $\text{V}_2\text{O}_5$ by $\text{KMnO}_4$	= 48.51% (complete oxidation)
0.1637 gr. gave 0.0259 gr. $\text{VO}_2$ by $\text{KMnO}_4$	= 15.82%

The analyses correspond tolerably well with the formula



which requires:

		Calc'd.		Found.
9 $\text{As}_2\text{O}_5$	2070	44.17	} 60.17	44.61
9 $\text{VO}_2$	750	16.00		15.82
8 $\text{V}_2\text{O}_5$	1461	31.17		31.17
4 $(\text{NH}_4)_2\text{O}$	208	4.44		4.12
11 $\text{H}_2\text{O}$	198	4.22		4.28 (diff.)
	4687	100.00		

The formula given must be doubled to give a structural scheme in which all the terms will be symmetrically arranged.

It appears at least probable that classes of antimonio-vanadates and antimonio-vanadico-vanadates also exist, but the few experiments which I have been able to make with the small quantity of material at my disposal are not conclusive as to either point, and I hope to be able to return to the subject.

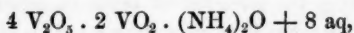
#### VANADICO-VANADATES.

Salts belonging to this series are formed when solutions of vanadates are mixed with those of vanadic dioxide, and when vanadates undergo partial reduction by the action of any reducing agent. These compounds are often crystalline and well defined. They have, usually at least, a green color.

**2 : 4 Ammonic Vanadico-vanadate.** — When a solution of vanadic dioxide in chlorhydric acid is added to one of ammonic metavanadate, a fine green crystalline salt separates, but slightly soluble in either cold or hot water. The salt analyzed was not recrystallized, but merely washed with cold water and dried upon woollen paper. Of this salt,

{ 1.0470 gr. gave 0.0159 gr. $\text{VO}_2$ by $\text{KMnO}_4$ = 15.21% $\text{VO}_2$
{ 1.0470 gr. " 0.0701 gr. $\text{V}_2\text{O}_5$ " = 66.98% $\text{V}_2\text{O}_5$
0.1470 gr. " 0.0066 gr. $(\text{NH}_4)_2\text{O}$ = 4.50%

The analyses lead to the formula

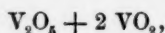


which requires

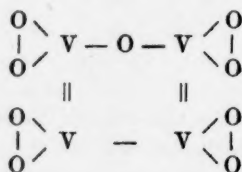
		Calc'd.	Found.
4 $\text{V}_2\text{O}_5$	730.4	66.82	66.98
2 $\text{VO}_2$	166.6	15.24	15.21
$(\text{NH}_4)_2\text{O}$	52	4.76	4.50
8 $\text{H}_2\text{O}$	144	13.18	13.31 (diff.)
	<hr/> 1093	<hr/> 100.00	

The following may serve as starting-points for further investigation. When solutions of sodic divanadate and manganous sulphate are mixed and allowed to stand in an open vessel, very dark green well-defined crystals are gradually deposited. There is here, doubtless, reduction from the presence of dust. When a solution of vanadic dioxide in chlorhydric acid is mixed with solutions of the sulphates of zinc, copper,

cobalt, or nickel, and of sodic divanadate, dark green crystalline precipitates are formed on standing, which would appear to be vanadico-vanadates, but which, as they are formed in the presence of an excess of a strong acid, may prove to be types of vanadico-vanadic acids. In his valuable paper on the salts formed by vanadic acid, Rammelsberg has described a remarkable compound, which may be regarded as an anhydride of a special form of vanadico-vanadic acid. This compound has the formula

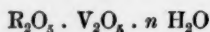


and forms black microscopic crystals. Its structural formula may be written:



It is easy to see how acids of various types might be derived from such anhydrides by replacing oxygen by an equivalent of hydroxyl. The existence of very well defined series of phosphoroso-tungstates and phosphoroso-molybdates, and of similar series of compounds containing  $\text{As}_2\text{O}_3$  and  $\text{Sb}_2\text{O}_3$ , would naturally lead to the attempt to form similar classes of complex acids containing  $\text{V}_2\text{O}_5$ . Want of material has prevented me from experimenting in this direction, and I must content myself with directing the attention of other chemists to the subject. Vanadic protoxide appears to possess the properties of a base only, but our knowledge of the subject is so imperfect that it may also be well worth while to determine whether there may not be a class of vanadium compounds corresponding to the hypophospho-tungstates and hypophospho-molybdates.

The existence of classes of phospho-vanadates and arsenio-vanadates embraced under the general formula



would seem to imply that of corresponding chlorides, bromides, etc., of corresponding or analogous types,



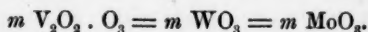
Various compounds of this kind have already been observed by chemists, though, so far as I am aware, no attempt has been made to classify

them or to assign to them their true position as double chlorides, etc., corresponding to double oxides capable of forming complex acids. Examples of this class are the following:—

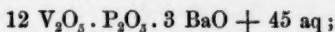
$\text{SnCl}_4$	+	$\text{PCl}_5$	Casselmann.
$\text{SnCl}_4$	+	$\text{POCl}_3$	"
$\text{TiCl}_4$	+	$\text{POCl}_3$	Weber.
$\text{TiCl}_4$	+	$\text{PCl}_5$	Tütschew.
$\text{SeCl}_4$	+	$\text{SbCl}_5$	Weber.
$\text{VOCl}_2$	+	$\text{PtCl}_4$	Brauner.
$\text{Al}_2\text{Cl}_6$	+	$2 \text{POCl}_3$	Casselmann.
$\text{Fe}_2\text{Cl}_6$	+	$2 \text{POCl}_3$	"
$\text{SbCl}_3$	+	$\text{PCl}_5$	Weber.
$\text{SbCl}_3$	+	$\text{POCl}_3$	"

It is at least possible that in these and many similar cases complex or double acids correspond to the double chlorides, and it is probable that the action of such double chlorides upon solutions of acid tungstates and molybdates would produce complex acids containing tungsten or molybdenum and the two acid-forming oxides corresponding to the two united chlorides. I shall at another time specially consider the compounds of platinous and phosphorous chlorides discovered by Schützenberger.

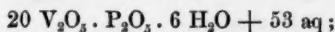
In my paper upon the vanadium compounds of tungsten and molybdenum I have endeavored to show that many formulas may be reduced to the same types as those of the phospho-tungstates and phospho-molybdates, provided that we assume that a part at least of the vanadic pentoxide is to be regarded as replacing tungstic or molybdic oxide, or that we have the chemical equivalence expressed by the equation



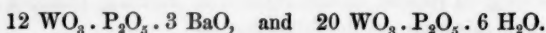
This hypothesis had the advantage of simplifying many formulas materially, but was wholly unsupported by any positive evidence. I have now shown that there exist classes of phospho-vanadates and arsenio-vanadates which do not contain tungstic or molybdic oxide, but which are exactly parallel to phospho-tungstates, vanadio-tungstates, etc. in composition. Thus we have the salt,



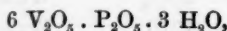
and the acid,



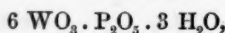
corresponding to



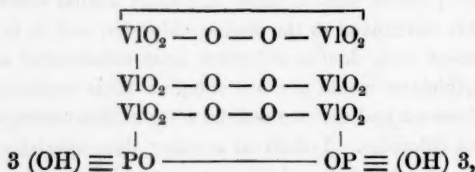
As regards the mode of replacement, however, our views must depend upon the special form of structural formulas which we provisionally adopt. With the view which I have taken of the subject, we may write for a phospho-vanadic acid assumed to have the formula



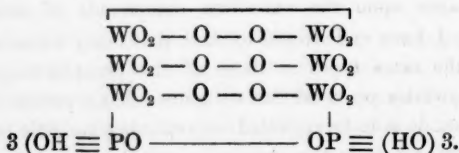
corresponding to the phospho-tungstic acid



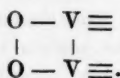
the structural formula,



exactly like

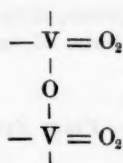


In the formula of the phospho-vanadic acid assumed, I have represented the complex  $\text{V}_2\text{O}_2$  by  $\text{Vl}$ ; and it is easy to see how, structurally, this may be regarded as hexatomic, and as replacing  $\text{W}^{\text{VI}}$  or  $\text{Mo}^{\text{VI}}$ , since we may reasonably suppose that we have

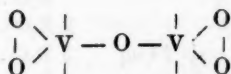


With this view of the subject  $(\text{V}_2\text{O}_2)_2 = \text{WO}_2 = \text{MoO}_2$ , etc. This mode of formulating compounds containing vanadic pentoxide enables us, as I have shown, to reduce many complex salts to relatively simpler types, and is supported, as we shall presently see, by the formulas of a special class of vanadates exactly corresponding to meta-

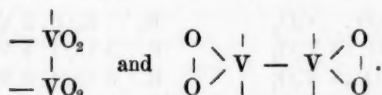
tungstates and metamolybdates. On the other hand, in by far the greater number of compounds thus far studied, the complex is to be regarded, I think, as built up of terms of the form  $\text{RO}_2$ , which may or may not be linked together by one or more atoms of oxygen. In certain cases, therefore, vanadic pentoxide may enter the complex with the structural formula



or as



This last view is strongly supported by the frequent presence of vanadic dioxide, two molecules of which may be considered as associated without a link of oxygen, as in the structural formulas



Finally, as I shall also prove, the structural formula must show what particular modification of phosphoric or vanadic oxide or acid is contained in the salt, since we have not merely ortho-phospho-tungstates but pyro-phospho-tungstates, various modifications of meta-phospho-tungstates, and corresponding compounds of molybdenum. It is at least probable that the different modifications of vanadic pentoxide or acid enter in a similar manner. These appear to be very numerous, and a wide field is thus opened for research. I shall return to this subject in the purely theoretical portion of my work.

If the view which I have taken as to the composition of the complex acids containing vanadium be correct, we ought to find some additional support for it in the constitution of the salts of vanadic acid. These have been studied by Roscoe, and especially by Norblad\* and by Rammelsberg,† but the results obtained by these chem-

\* Bidrag till kännedomen om Vanadiums Amfidsalter. Upsala Universitets Årsskrift, 1873.

† Sitzungsberichte der Königl. Preuss. Akademie der Wissenschaften, 1883, p. 1.

ists have not been systematized. The very numerous vanadates may be arranged, as I find, under seven groups or series. These are here given for the sake of comparison, typical salts actually obtained in each series being marked by the initials of the analysts. The existence of salts corresponding to other general formulæ is a matter of inference only. As will be seen at once, the first series corresponds to the group of metatungstates, if we compare  $V_2O_2 \cdot O_3$  with  $WO_3$ . Terms 1 and 3 of this series of vanadates have twice the usually given molecular weights.

## FIRST SERIES.

Vanadates.	Metatungstates.
$R_2O \cdot 4 V_2O_5$	$R_2O \cdot 4 WO_3$
R. $2 K_2O \cdot 6 V_2O_5$	$2 R_2O \cdot 6 WO_3$
N. $3 Na_2O \cdot 8 V_2O_5 + 24 aq$	$3 R_2O \cdot 8 WO_3$
R. $4 Na_2O \cdot 10 V_2O_5 + 14 aq$	$4 R_2O \cdot 10 WO_3$
$5 R_2O \cdot 12 V_2O_5$	$5 R_2O \cdot 12 WO_3$

## SECOND SERIES.

N. $Na_2O \cdot V_2O_5$
R. $2 K_2O \cdot 3 V_2O_5$
R. $3 Li_2O \cdot 5 V_2O_5$
$4 R_2O \cdot 7 V_2O_5$

## THIRD SERIES.

R. $K_2O \cdot 2 V_2O_5 + 4 aq$
R. $3 Li_2O \cdot 4 V_2O_5 + 12 aq$
R. $5 Li_2O \cdot 6 V_2O_5 + 30 aq$
$7 R_2O \cdot 8 V_2O_5$

## FOURTH SERIES.

R. $3 Li_2O \cdot 2 V_2O_5 + 15 aq$
$4 R_2O \cdot 4 V_2O_5$
$5 R_2O \cdot 6 V_2O_5$
$6 R_2O \cdot 8 V_2O_5$

## FIFTH SERIES.

R. $2 K_2O \cdot V_2O_5 + 3 aq$
$3 R_2O \cdot 3 V_2O_5$
$4 R_2O \cdot 5 V_2O_5$
$5 R_2O \cdot 7 V_2O_5$

## SIXTH SERIES.

$4 R_2O \cdot 2 V_2O_5$
R. $5 K_2O \cdot 4 V_2O_5 + 7 aq$
$6 R_2O \cdot 6 V_2O_5$
$7 R_2O \cdot 8 V_2O_5$

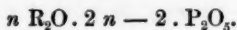
## SEVENTH SERIES.

Ro. $3 Na_2O \cdot V_2O_5 + 16 aq$
$4 R_2O \cdot 3 V_2O_5$
$5 R_2O \cdot 5 V_2O_5$
$6 R_2O \cdot 7 V_2O_5$

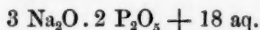
The seven series which I have given embrace, I believe, all known types of vanadates. Each series may be represented by a general formula expressing the relation between the number of molecules of acid and basic oxides. These general formulæ are:

- I.  $n \text{ R}_2\text{O} . 2 n + 1 . \text{V}_2\text{O}_5$   
 III.  $n \text{ R}_2\text{O} . n + 1 . \text{V}_2\text{O}_5$   
 II.  $n \text{ R}_2\text{O} . 2 n - 1 . \text{V}_2\text{O}_5$   
 ?  $n \text{ R}_2\text{O} . 2 n - 2 . \text{V}_2\text{O}_5$   
 V.  $n \text{ R}_2\text{O} . 2 n - 3 . \text{V}_2\text{O}_5$   
 IV.  $n \text{ R}_2\text{O} . 2 n - 4 . \text{V}_2\text{O}_5$   
 VII.  $n \text{ R}_2\text{O} . 2 n - 5 . \text{V}_2\text{O}_5$   
 VI.  $n \text{ R}_2\text{O} . 2 n - 6 . \text{V}_2\text{O}_5$

The arrangement here given makes it probable that at least one series remains to be discovered. Fleitmann and Henneberg have described a phosphate having the formula  $6 \text{ Na}_2\text{O} . 5 \text{ P}_2\text{O}_5$ . Such a compound would belong to a class of phosphates represented by the general formula — wanting among the vanadates —



Roscoe long since established the correspondence of the vanadates and phosphates up to a certain limit. Further investigation is required to show how complete the correspondence is. From an examination of the terms in the seven series of vanadates given above, it will appear that various isomeric modifications are probable among vanadates, and that these correspond, in *form* at least, to the various metaphosphates, — mono, di, tri, tetra, and hexa-metaphosphates of Fleitmann and Henneberg. These chemists have also described a class of phosphates corresponding to the first term of the fourth series of vanadates given above. The sodium salt has the formula



In the imperfect state of our knowledge, all such coincidences are worthy of attention. Another conclusion may perhaps be safely drawn from the systematic arrangement of the vanadates which I have given. This is that meta, pyro, and ortho-vanadates, and the similar compounds of phosphorus, arsenic, antimony, etc., are not *isolated*, but are terms of more complete series. Thus the fifth series embraces the pyro-vanadates and their homologues, while the ortho-vanadates form the first term of the seventh series. In all the series given except the third, the common difference or homologizing term is  $\text{R}_2\text{O} . 2 \text{ V}_2\text{O}_5$ ; in the third series, it is  $2 \text{ R}_2\text{O} . 2 \text{ V}_2\text{O}_5$ . In some cases only particular terms may exist to represent an entire series, because the special conditions necessary for the stability of other terms may be absent as regards degree. Taking now into account

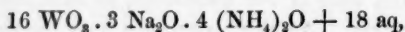
the analogy which I have shown to exist between  $V_2O_5 \cdot O_3$  and  $WO_3$  or  $MoO_3$ , we may perhaps extend the above conclusions to the cases of the tungstates, molybdates, chromates, etc. Thus we may regard  $K_2O \cdot 2 CrO_3$  as the initial term of a series corresponding to the third series of vanadates. If we double the usual formula of potassic tetrachromate, and write it  $2 K_2O \cdot 6 CrO_3$ , we shall have the second term in a series corresponding to that of the metatungstates, the first term being the tetrachromate  $K_2O \cdot 4 CrO_3$ .

As a further support to my view that the metatungstates form a homologous series, I shall here describe two new tungstates obtained since the first part of this work was published.

16:3:4 *Sodio-ammonic Tungstate*.—I obtained this salt accidentally in attempting to prepare a series of glycono-phospho-tungstates. The thick syrupy liquid obtained by heating pulverized glacial phosphoric acid with glycerine, and allowing the mixture to stand for some days, was neutralized with ammonia and poured into a hot solution of 12:5 sodic tungstate. A beautiful white salt, in shimmering talcose scales, separated as the solution cooled. After careful draining, the salt was recrystallized for analysis. The crystals had a fatty lustre, and were quite easily soluble in hot water. No phosphoric acid could be found in the salt by the most careful testing, and no organic matter. In this salt,

2.3796 gr. lost on ignition	0.2825 gr.	= 11.87 %
2.1691 gr. " "	0.2568 gr.	= 11.84 %
2.1691 gr. gave	1.8209 gr. $WO_3$	= 83.94 %
2.0956 gr. " "	0.0973 gr. $(NH_4)_2O$	= 4.64 %

The analyses correspond to the formula



which requires:

		Calc'd.	Found.
16 $WO_3$	3712	83.79	83.94
3 $Na_2O$	186	4.20	4.21 (diff.)
4 $(NH_4)_2O$	208	4.69	4.64
18 $H_2O$	324	7.32	7.21
	4430	100.00	

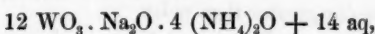
This salt is especially interesting because it supplies a new term to the series of metatungstates, — the highest as yet obtained.

12:1:4 *Sodio-ammonic Tungstate*. — This salt was obtained accidentally in an attempt to prepare a series of ethylo-phospho-tungstates. Syrupy phosphoric acid and absolute alcohol were mixed and heated for half an hour to about 80° C., and the mixture allowed to stand twenty-four hours. Ammonia was then added in small quantities at a time until in excess, the liquid being kept cool, the object being to form an ammonic ethylo-phosphate. The solution was then poured into one of 12:5 sodic tungstate. After a few minutes an abundant precipitation took place of small shimmering scales, which were drained on the filter-pump, washed with cold water, then dissolved in hot water and filtered. A very small quantity of a very insoluble salt in scales remained undissolved. The filtrate soon gave an abundance of small talcose scales with a fatty lustre.

Of this salt,

1.0293 gr. lost on ignition	0.1399 gr.	= 13.60 %
1.3019 gr. " "	0.1766 gr.	= 13.57 %
1.0001 gr. gave	0.0618 gr. (NH <sub>4</sub> ) <sub>2</sub> O	= 6.18 %
1.0293 gr. " "	0.8689 gr. WO <sub>3</sub>	= 84.46 %

The analyses correspond to the formula



which requires :

		Calc'd.	Found.
12 WO <sub>3</sub>	2784	84.22	84.46
Na <sub>2</sub> O	62	1.87	1.94 (diff.)
4 (NH <sub>4</sub> ) <sub>2</sub> O	208	6.29	6.18
14 H <sub>2</sub> O	252	7.62	7.42
	<u>3306</u>	<u>100.00</u>	

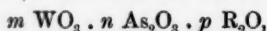
No trace of phosphoric acid could be detected in the salt, which is perhaps only interesting as furnishing additional evidence of the existence of a class of meta-tungstates in which the ratio of the tungstic oxide to the oxygen of the base is as 12:5. In this, as in the 16-atom salt above described, the presence of an excess of free ammonia explains the absence of phosphoric oxide in the compound formed.

My work on the compounds of vanadium is far less complete and thorough than I could have wished, on account of the relatively very high cost of the material. I indulge the hope that what I have done

will be found at least substantially correct, and that the whole subject will soon receive the attention of other chemists, who may have a more abundant supply of vanadium salts at their disposal.

#### ARSENOSO-TUNGSTATES.

The alkaline salts belonging to this series are easily prepared by boiling arsenous oxide with strong solutions of acid tungstates, as, for example, with 12 : 5 or 10 : 4 sodic salt. The arsenous oxide should be in excess to secure complete saturation. The filtered solution on standing usually deposits crystals of arsenous oxide in greater or less quantity. The salts of this series are either colorless or pale yellow. They are not very easily oxidized in acid solutions, but in presence of an excess of alkali they absorb oxygen from the air and are converted into arsenio-tungstates. Bromine and chlorine readily oxidize such solutions. The arsenoso-tungstates are, as a rule, more soluble than arsenio-tungstates. They are very stable and well defined, and may as a class be embraced under the general formula



in which  $n$  is usually greater than unity.

*Analytical Methods.* — Hydric sulphide precipitates arsenous sulphide from these salts, and usually without sensible reduction of the tungstic teroxide. It is best to precipitate from a hot solution, and to pass the current of the gas for a long time to insure complete decomposition. The arsenous sulphide may then be collected and weighed upon a Gooch asbestos filter. The tungstic oxide may be determined in the filtrate by mercurous nitrate in the usual manner. The simplest and most satisfactory method of determining the arsenic is by titration with iodine in a solution containing an excess of sodic or potassic bicarbonate. Finally, it is possible to determine the arsenic by oxidizing the solution with bromine after adding an excess of an alkaline carbonate, and then precipitating the arsenic in the form of ammonio-magnesian arsenate. The precipitate must be redissolved in dilute chlorhydric acid and precipitated a second time.

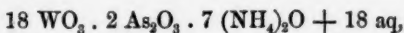
The alkaline arsenoso-tungstates are, as a rule, easily soluble; the crystalline salts are often soft and gummy, though well defined. They appear in some cases to be decomposed more or less completely by solution and evaporation, with separation of arsenous oxide and formation of new salts of different series. In certain cases the addition of a salt of one of the heavy metals determines the precipitation of crystals

of arsenous oxide in quantity. It is well known that alkaline hydrates also dissolve arsenous oxide in a proportion more than sufficient to form definite salts, and that the solutions deposit crystals of arsenous oxide on standing.

9:1 *Ammonic Arsenoso-tungstate*. — A boiling strong solution of 12:5 sodic tungstate dissolves arsenous oxide very readily, and in large quantity. The solution on evaporation gives a colorless or very pale yellow thick gummy mass, which on re-solution leaves octahedral crystals of arsenous oxide. The solution of the sodic salt gives with ammonic chloride, after standing some time, beautiful pale yellow almost colorless prisms. These may be redissolved and recrystallized without decomposition. Of this salt,

1.2699 gr. lost on ignition 0.2750 gr. = 21.65%  $\text{H}_2\text{O}$ ,  $\text{As}_2\text{O}_3$ , and  $\text{NH}_3$   
 1.3508 gr. gave by titration with iodine 0.1034 gr.  $\text{As}_2\text{O}_3$  = 7.65%  
 1.9457 gr. " 0.2713 gr.  $\text{NH}_4\text{Cl}$  = 6.78%  $(\text{NH}_4)_2\text{O}$   
 0.9776 gr. " 0.7732 gr.  $\text{WO}_3$  = 79.09% by  $\text{Hg}_2(\text{NO}_3)_2$  and ignition.

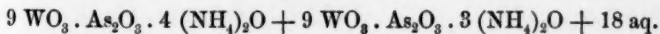
The analyses lead to the formula



which requires:

		Calc'd.	Found.
18 $\text{WO}_3$	4176	79.39	79.09
2 $\text{As}_2\text{O}_3$	396	7.53	7.65
7 $(\text{NH}_4)_2\text{O}$	364	6.92	6.78
18 $\text{H}_2\text{O}$	324	6.16	6.48
	<hr/> 5260	<hr/> 100.00	

The salt may of course be regarded as a double salt, but in this class of salts, as in the arsenio-tungstates and phospho-tungstates, I am disposed to think that in all cases we have an even number of molecules of tungstic oxide united with at least *two* molecules of arsenous oxide. Further investigations are of course required to settle this question. Meantime, from the analogy of the baric salt, we may write the formula provisionally as

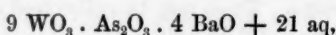


9:1 *Baric Arsenoso-tungstate*. — A solution of sodic arsenoso-tungstate obtained as above gives a white crystalline precipitate with baric chloride which is nearly insoluble in water, and which was there-

fore only washed upon the filter and dried on woollen paper for analysis. In this salt,

1.1037 gr. ignited with  $\text{WO}_4\text{Na}_2$  lost 0.1290 gr. = 11.69%  $\text{H}_2\text{O}$   
 1.9764 gr. titrated with iodine gave 6.15%, 6.38%, 6.18%  $\text{As}_2\text{O}_3$ ,  
                     mean 6.23%  
 1.5652 gr. gave 0.4358 gr.  $\text{SO}_4\text{Ba}$  = 18.28%  $\text{BaO}$ .

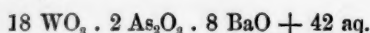
In determining the arsenous oxide the salt was first dissolved in very dilute chlorhydric acid, an excess of sodic bicarbonate being added before titration. The analyses correspond with the formula



which requires:

		Calc'd.	Found.
9 $\text{WO}_3$	2088	63.74	63.80
$\text{As}_2\text{O}_3$	198	6.04	6.23
4 $\text{BaO}$	612	18.68	18.28
21 $\text{H}_2\text{O}$	378	11.54	11.69
	<hr/> 3276	<hr/> 100.00	

The formula may be



I have stated above that arsenoso-tungstates pass readily into arsenio-tungstates by oxidation and assumption of two additional atoms of oxygen. It seemed therefore natural to suppose that other simple or complex molecules might also be added to the molecule of arsenous oxide entering into the complex acid. I shall hereafter give the results of a detailed examination of this subject.

16:8 *Sodic Arsenoso-tungstates*. — Arsenous oxide dissolves readily in 10:4 sodic tungstate on boiling. When an excess of arsenic is present, the filtrate, after evaporation to the consistency of a syrup, deposits on spontaneous evaporation large colorless prismatic crystals. These dissolve readily in water without decomposition and may be recrystallized until perfectly pure. After four recrystallizations,

0.9451 gr. gave with  $\text{CO}_3\text{NaH}$  and iodine 0.2178 gr.  $\text{As}_2\text{O}_3$  = 23.05%  
 0.6128 gr.   "                   "                   "   0.1416 gr.   "   = 23.10%  
 1.1327 gr. gave 0.3237 gr.  $\text{As}_2\text{S}_3$  = 23.01%  $\text{As}_2\text{O}_3$   
 0.9225 gr.   "   0.5005 gr.  $\text{WO}_3$  = 54.26%  
 1.0614 gr.   "   0.5781 gr.   "   = 54.46%  
 0.8517 gr.   "   0.1238 gr.  $\text{H}_2\text{O}$  = 14.54%

The analyses agree well with the formula



which requires:

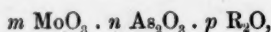
		Calc'd.		Found.	
16 $\text{WO}_3$	3712	54.23	54.28	54.46	
8 $\text{As}_2\text{O}_3$	1584	23.14	23.05	23.10	23.01
9 $\text{Na}_2\text{O}$	558	8.16		8.04 (diff.)	
55 $\text{H}_2\text{O}$	990	14.47		14.54	
	<hr/> 6844	<hr/> 100.00			

The salt gives off vapors of arsenous oxide even on gentle heating, and the determination of the water cannot be made by the use of sodic tungstate. After many trials, it was found best to mix the salt in a porcelain boat with plumbic oxide and carefully heat in a combustion tube, collecting the water in asbestos drenched with sulphuric acid. This process, suggested by my assistant, Mr. Herman Schmidt, gave good results in this case. A solution of the salt gives white flocky crystalline precipitates with baric, strontic, and calcic chlorides. Mercurous nitrate gives a pale yellow precipitate, which becomes darker on heating, and finally takes a dirty greenish-white color. Argentic nitrate gives a milk-white precipitate, which remains suspended for a long time. Manganous sulphate gives no precipitate, but the solution becomes yellow, and after standing some time yields beautiful bright yellow tabular crystals. Ammonic and potassic arsenates and orthophosphates give white crystalline precipitates, which appear to be respectively arsenoso-arsenio-tungstates and arsenoso-phospho-tungstates. The mother liquor of the 16 : 8 salt gives on evaporation a few crystals in a thick colorless syrup, which, after a few days, forms a pale yellowish hard gummy mass. This may prove to contain a second arsenoso-tungstate. The best method of preparing the beautiful 16 : 8 salt in quantity will probably be to mix 12 : 5 or 10 : 4 sodic tungstate and arsenous oxide in the precise ratio indicated by the formula of the salt, and, after adding water, to boil until the arsenous oxide is dissolved.

#### ARSENOSO-MOLYBDATES.

Arsenoso-molybdates are formed under the same conditions as arsenoso-tungstates, by boiling solutions of acid molybdates with an excess of arsenous oxide. In this case also there is always a sort of

supersaturation, and arsenous oxide separates from the solution on cooling. The general statements made concerning the arsenoso-tungstates apply to these salts also. The general formula is



in which  $n$  is usually greater than unity. The salts are often beautifully crystalline.

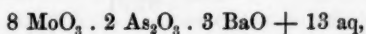
*Analytical Methods.* — Arsenous oxide may be determined in these salts by oxidizing the solutions in presence of an excess of an alkaline carbonate by means of bromine, and precipitating as ammonio-magnesian arsenate. The precipitation must be repeated a second time, but the final treatment with ammoniac sulphide, which I have recommended for the separation of phosphoric and molybdic oxides, is of course inadmissible. By far the best method of determining the arsenic in these salts is titration with iodine after addition of an excess of an alkaline bicarbonate. It is not possible to determine the oxides of molybdenum and arsenic together by precipitation with mercurous nitrate, since no amount of care suffices to prevent the volatilization of arsenic in the subsequent ignition. For the same reason, it is also very difficult to determine the water of crystallization by the ignition loss, as fumes of arsenous oxide are given off at temperatures which are much below that at which sodic tungstate fuses. The degree of facility with which this takes place varies with the salt to be analyzed. As regards the determination of the water, I have found it best to heat gently in a porcelain crucible, supported over a small iron cup heated from below, but even in this case the results are never very satisfactory. Arsenous oxide cannot be separated from molybdic oxide by hydric sulphide, since molybdic sulphide is always precipitated at the same time, even when phosphoric acid has been added in excess. I have, however, found that fairly good determinations of molybdic oxide may be made in many cases by dissolving, boiling with a small excess of ammonia, adding a little ammoniac chloride, and finally precipitating with baric chloride. The baric molybdate may then be ignited and weighed upon an asbestos filter. The results, if not very accurate, are at least sufficiently close to be of great service as verifications of formulas.

8 : 2 *Baric Arsenoso-molybdate.* — A boiling strong solution of 14 : 6 ammoniac molybdate dissolves arsenous oxide in large quantity, and very readily. The solution has usually a yellowish-green color from slight reduction of the molybdic tetroxide. After filtration and evaporation upon a water-bath, it deposits an abundance of octahedral crys-

tals of arsenous oxide. The filtrate from these does not yield crystals on standing, but after evaporation upon the water-bath solidifies to a greenish gummy mass, readily soluble in water, often however leaving a residue of arsenous oxide. The solution of this gummy salt gives a white crystalline precipitate with baric chloride. The filtrate from this, after evaporation and standing, yields an abundance of beautiful very pale greenish crystals, which may be redissolved and recrystallized without decomposition. In this salt,

1.1230 gr. lost on heating	0.1126 gr. = 10.03%
1.0548 gr. gave	0.3258 gr. $\text{SO}_4\text{Ba}$ = 20.28% $\text{BaO}$
0.3919 gr. "	0.0678 gr. $\text{As}_2\text{O}_3$ = 17.31%
0.5774 gr. "	0.0995 gr. " = 17.23%
0.9729 gr. "	1.0383 gr. $\text{MoO}_4\text{Ba}$ = 51.74% $\text{MoO}_3$

The analyses lead to the formula



which requires :

		Calc'd.		Found.	
8 $\text{MoO}_3$	1152	51.41	} 69.08	51.74	} 69.01
2 $\text{As}_2\text{O}_3$	396	17.67		17.31	
3 $\text{BaO}$	459	20.48		20.28	
13 $\text{H}_2\text{O}$	234	10.44		10.03	
	2241	100.00		99.32	

The arsenous oxide was determined in the first analysis by boiling with a solution of sodic dicarbonate, filtering, and titrating with iodine; in the second, by direct titration without previous filtration. The baryta was separated by fusion with sodic carbonate, and weighed as sulphate. The water was found by heating over a radiator until a constant weight was obtained, as it was impossible to ignite with sodic tungstate without volatilization of arsenous oxide.

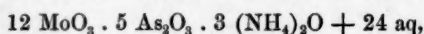
The salt requires a very large quantity of water for solution. The dry salt in fine powder boiled with argentic nitrate gives a beautiful yellow crystalline salt. Thallous nitrate yields, under the same circumstances, a very pale yellow, also crystalline salt. The mercurous salt is pale yellow, but not distinctly crystalline.

12 : 5 *Arsenoso-molybdate of Ammonium*. — When a solution of zincous sulphate is added to one of the gummy arsenoso-molybdate of ammonium, no precipitate is found at first, but after a time colorless

crystals are formed which do not contain zinc, and which may be recrystallized without apparent decomposition. The salt dissolves in a large quantity of water to a colorless solution. It is only partially decomposed by boiling with mercurous nitrate. In this compound,

0.7105 gr.	gave 0.0326 gr. $(\text{NH}_4)_2\text{O}$	= 4.58%
0.9785 gr.	" 0.0455 gr. "	= 4.65%
1.2612 gr.	" 1.3720 gr. $\text{MoO}_4\text{Ba}$	= 52.74% $\text{MoO}_3$
1.3081 gr.	" 0.3856 gr. $\text{As}_2\text{O}_3$	= 29.48%
0.6044 gr.	" 0.1787 gr. "	= 29.55%

The analyses correspond fairly well with the formula



which requires:

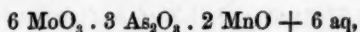
		Calc'd.		Found.	
12 $\text{MoO}_3$	1728	52.28	} 82.21	52.74	} 82.24
5 $\text{As}_2\text{O}_3$	990	29.94		29.48	
3 $(\text{NH}_4)_2\text{O}$	156	4.71		4.58	4.65
24 $\text{H}_2\text{O}$	432	13.07		13.15	
	3306	100.00			

The reactions of this salt were studied by acting with metallic solutions upon the finely pulverized substance, so as to avoid, if possible, the decomposing action of water. In this manner cold solutions of argentic and thalious nitrates give beautiful colorless granular crystals. Baric chloride gives a white colorless salt more flocky than the ammonium compound. Manganous sulphate does not react in the cold, but on boiling for some time a beautiful pale canary-yellow crystalline salt is formed. Cupric sulphate does not act when cold, but on boiling a clear solution results.

*6:3 Arsenoso-molybdate of Manganese.* — A portion of the dry gummy mass of arsenoso-molybdate of ammonium, which had stood for some time in the laboratory, was redissolved and filtered from a small quantity of arsenous oxide. The filtrate gave no precipitate with manganous sulphate, but, on boiling, the fine green solution became much lighter in color, then turbid, and finally deposited very beautiful bright orange-colored octahedral crystals insoluble in water. Of this salt,

0.5961 gr.	gave 0.2052 gr. $\text{As}_2\text{O}_3$	= 34.41%
0.7341 gr.	" 0.1216 gr. $\text{P}_2\text{O}_5\text{Mn}_2$	= 8.28% $\text{MnO}$
0.6362 gr.	lost on heating over a radiator 0.0428 gr.	= 6.73%

The analyses correspond to the formula



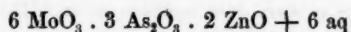
which requires :

		Calc'd.	Found.
6 MoO <sub>3</sub>	864	50.59	50.58
3 As <sub>2</sub> O <sub>3</sub>	594	34.78	34.41
2 MnO	142	8.31	8.28
6 H <sub>2</sub> O	108	6.32	6.73
	1708	100.00	

The molybdic oxide was determined by difference only. By mixing a solution of the gummy arsenoso-molybdate of ammonium with solutions of zincous and cupric sulphates respectively, after standing, beautiful octahedral crystals were deposited, which in the case of the zinc salt were colorless, in that of copper, of a fine green. The corresponding nickel salt was also in beautiful green octahedral crystals. In the zinc salt,

0.2378 gr.	gave 34.52%	As <sub>2</sub> O <sub>3</sub>	by titration with iodine.
0.3115 gr.	" 34.47%	"	" "
0.2169 gr.	" 34.56%	"	" "

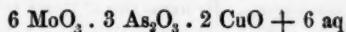
The formula



requires 34.38%. In the copper salt,

0.2619 gr.	gave 34.67%	As <sub>2</sub> O <sub>3</sub>	by titration with iodine.
0.2006 gr.	" 34.89%	"	" "

The formula



requires 34.41%.

In the cases of both the zinc and copper salts a trace of free arsenous oxide was probably mixed with the salt analyzed. The nickel salt doubtless corresponds to the other three. In the case of the manganese salt, fumes of arsenous oxide were given off at very low temperatures. The pale canary-yellow manganese salt obtained by precipitating the 12 : 5 ammoniac salts with manganous sulphate corresponded to the formula



0.1727 gr. gave 31.77, 31.62, and 31.73%  $\text{As}_2\text{O}_3$  by titration with iodine.  
1.1393 gr. " 0.0898 gr.  $\text{Mn}_3\text{O}_4 = 7.33\%$   $\text{MnO}$ .

The formula given requires 31.77%  $\text{As}_2\text{O}_3$  and 7.59%  $\text{MnO}$ . The salt gave off arsenous oxide very freely when heated with sodic tungstate.

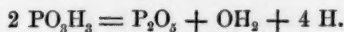
#### PHOSPHOROSO-TUNGSTATES.

I have already described the class of phosphoroso-molybdates, and will now consider the parallel group of phosphoroso-tungstates. The alkaline salts of this series are readily formed by the action of phosphorous and chlorhydric acids upon metatungstates of the higher order. They are, as a rule, better defined than the corresponding phosphoroso-molybdates, and are in all probability very numerous. The compounds to be described will be sufficient to open the subject for further investigation. The analytical methods employed were the same as in the case of the corresponding molybdenum salts, except that after oxidation of phosphorous to phosphoric acid, tungsten and phosphorus were usually precipitated together by mercurous nitrate and mercuric oxide.

22:4:6 *Ammonic Phosphoroso-tungstate*. — When the solution of phosphorous and chlorhydric acids formed by the action of water upon phosphoric terchloride is poured upon crystalline 12:5 ammonic tungstate, the salt packs at once into a dense mass. This is to be well rubbed up in a mortar with a large excess of the acid liquid, and allowed to stand for twenty-four hours. The greater part of the mass then presents large granular colorless crystals. A much smaller proportion of a white fine-grained salt is formed at the same time, and is easily separated by washing from the heavier crystals of the granular salt. This last may be washed with cold water on the filter pump, and dried on woollen paper. In mass the crystals present a faint but distinct tinge of yellow. The salt is but slightly soluble in cold water, but dissolves in a rather large proportion of boiling water to a yellow liquid. The solution gives no precipitate with cupric sulphate, but the mixed liquid becomes somewhat darker on boiling. With argentic nitrate it gives a turbid solution, which becomes purplish on heating, and finally gives a dark dull-purple precipitate. With mercurous nitrate the solution gives a white light precipitate, which becomes deep yellow on heating, and regains its white color on cooling. In this salt,

1.6407 gr. gave 0.1136 gr. $P_2O_7Mg_2$	=	5.12%	$PO_3H_3$
1.7666 gr. " 0.1256 gr. "	=	5.26%	"
1.5933 gr. " 0.0791 gr. $(NH_4)_2O$	=	4.96%	
1.7340 gr. lost with $WO_4Na_2$ 0.2253 gr.	=	12.99%	

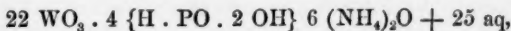
The analysis is of course subject to the corrections indicated by the equation



The results agree very well with the formula



or



which requires:

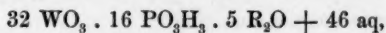
		Calc'd.	Found.
22 $WO_3$	5104	82.40	82.46
4 $PO_3H_3$	328	5.29	5.26 5.12
6 $(NH_4)_2O$	312	5.04	4.96
25 $H_2O$	450	7.27	7.32
	<hr/> 6194	<hr/> 100.00	

The phosphorous acid was oxidized by bromine after adding an excess of sodic carbonate. The salt is quietly decomposed by heating, giving a mixture of  $WO_3$  .  $W_2O_5$  and  $P_2O_5$ .

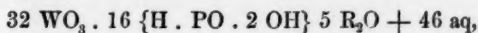
32 : 16 : 5 *Potassic Phosphoroso-tungstate*.— This salt was formed, like the ammonium salt, by the action of a mixture of phosphorous and chlorhydric acids upon crystallized 10 : 4 potassic tungstate. In this case, also, two salts appear to be formed, — a heavier colorless crystalline salt in relatively large quantity, and a lighter fine-grained salt easily removed by careful washing. Of these, only the first was examined. Of this salt,

1.4225 gr. gave 1.2124 gr. oxides	=	85.23%	$WO_3 + P_2O_5$
1.3877 gr. " 0.2428 gr. $P_2O_7Mg_2$	=	11.19%	$P_2O_5$
1.3949 gr. lost 0.1406 gr.	=	10.08%	$PO_3H_3$

The analyses correspond to the formula



or



which requires :

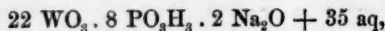
		Calc'd.	Found.
32 $\text{WO}_3$	7424	73.97	74.04
16 $\text{PO}_3\text{H}_3$	1312	13.07	12.96
5 $\text{R}_2\text{O}$	472	4.70	4.69 (diff.)
46 $\text{H}_2\text{O}$	828	8.26	8.31
	<hr/> 10036	<hr/> 100.00	

The salt is but slightly soluble even in boiling water. It has no yellow tint.

22 : 8 : 2 *Sodic Phosphoroso-tungstate*. — This salt was formed, like the last, by the action of a mixture of phosphorous and chlorhydric acids upon crystallized 10 : 4 sodic tungstate. The action is very energetic. The colorless crystals of the tungstate soon disappear, and are replaced by yellow granular crystals in large quantity. The yellow crystals were well washed upon the filter-pump with cold water, and dried on woollen paper. Of this salt,

1.7082 gr. gave 1.4895 gr. oxides = 87.19 %  $\text{WO}_3 + \text{P}_2\text{O}_5$   
 1.3623 gr. " 0.1870 gr.  $\text{P}_2\text{O}_5 \cdot \text{Mg}_2$  = 8.78 %  $\text{P}_2\text{O}_5$  = 10.15 %  $\text{PO}_3\text{H}_3$   
 1.3532 gr. lost with  $\text{WO}_4\text{Na}_2$  0.1481 gr. = 10.94 %

The analyses correspond to the formula



which requires :

		Calc'd.	Found.
22 $\text{WO}_3$	5104	78.36	78.40
8 $\text{PO}_3\text{H}_3$	656	10.07	10.15
2 $\text{Na}_2\text{O}$	124	1.90	1.87 (diff.)
25 $\text{H}_2\text{O}$	630	9.67	9.58
	<hr/> 6514	<hr/> 100.00	

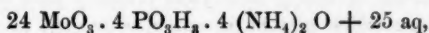
The sodium salt is nearly insoluble in cold water, and but slightly soluble in boiling water. The undissolved portion takes a much brighter yellow color. As in the cases of the potassium and ammonium salts, a small quantity of a second salt, in very small crystals and of a white color, is formed at the same time.

PHOSPHOROSO-MOLYBDATES (*again*).

As the phosphoroso-molybdate of ammonium, which I have described in another part of this paper, appeared to contain a trace of phosphoric acid, I repeated the preparation with a perfectly pure solution of phosphorous acid obtained by the action of water upon phosphorous chloride. The liquid contained, of course, free chlorhydric acid, and was poured into a cold strong solution of 14:6 ammonic molybdate. A sulphur-yellow precipitate was at once formed, consisting of very minute talcose scales. The salt was washed on the filter-pump very thoroughly with cold water, and dried on woollen paper. It is readily soluble in hot water to a yellow liquid. The solution on boiling reduces mercuric chloride to mercurous chloride. It gives an abundant white, flocky precipitate with argentic nitrate, which on long boiling becomes darker. Finally, silver is reduced. In this preparation,

0.7247 gr. lost with $\text{WO}_4\text{Na}_2$	0.1150 gr. = 15.87 %
0.8323 gr. gave $(\text{NH}_4)_2\text{O}$	= 4.64 %
0.7426 gr. " 0.0776 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 6.68 % $\text{P}_2\text{O}_5$
0.9517 gr. " 0.0994 gr. "	= 6.68 % "

The phosphorous acid was oxidized by bromine in presence of an excess of  $\text{CO}_3\text{NaH}$ . The analyses correspond most nearly to the formula



which requires :

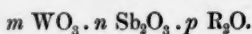
		Calc'd.		Found.
24 $\text{MoO}_3$	3456	77.80	} 85.18	77.45
4 $\text{PO}_3\text{H}_3$	328	7.38		7.71
4 $(\text{NH}_4)_2\text{O}$	208	4.68	} 14.82	4.64
25 $\text{H}_2\text{O}$	450	10.14		10.20
	4442	100.00		

The analyses confirm the formula first obtained, though the new salt contains eight molecules more of water of crystallization.

## ANTIMONOSO-TUNGSTATES.

When solutions of an acid tungstate of sodium are boiled with antimonious oxide, the latter very slowly dissolves, and it is difficult to obtain perfectly saturated solutions. It is best to employ antimonious

oxide which has been freshly precipitated from the corresponding chloride by sodic carbonate and washed by decantation with cold water. If the precipitated oxide is allowed to stand for some time, it becomes crystalline, and is then no longer available. The solution of antimonoso-tungstate obtained in this manner has a yellow color, and there is no sensible reduction of tungstic teroxide. Instead of this process, the following may be employed with advantage. Freshly precipitated antimonious oxychloride,  $\text{SbOCl}$ , after washing with cold water, dissolves very readily in boiling solutions of alkaline tungstates of the metatungstic series. The solutions obtained in this way are also yellow. The oxychloride, on standing for some days, also becomes highly crystalline, and then dissolves with great difficulty. The solutions of sodic salts obtained as above become on evaporation thick and syrupy, and finally yield yellow gummy masses. There is in these cases also a tendency to supersaturation, as with the arsenoso-tungstates, though by no means to the same extent, and crystals of antimonious oxide (hydrate?) are sometimes deposited. The concentrated solution of the sodic salt obtained as above gives yellow oils with strong solutions of potassic or ammonic salts, which are but slightly soluble in a large excess of the latter. After pouring off the supernatant liquid, the oils may be redissolved in a small quantity of water, and again precipitated by a large excess of a concentrated solution of a potassic salt. I prefer for this purpose the bromide. Two or three repetitions of this process yield a nearly pure potassic antimonoso-tungstate, which may be advantageously used in the preparation of other salts. The alkaline salts of this series are either oily liquids or gummy masses with a pale yellow color, and very easily soluble. The solutions absorb oxygen rather slowly from the air, and are not easily oxidized by bromine or chlorine unless in presence of an excess of alkali, as, for example, sodic bicarbonate. They then pass into antimonio-tungstates. The general formula of the antimonoso-tungstates is



*Analytical Methods.* — The quantitative separation of antimony from tungsten in these compounds may be effected by the following methods. Hydric sulphide passed through the solution previously acidulated with chlorhydric acid precipitates antimonious sulphide completely, without any sensible reduction or precipitation of tungsten. An aliquot portion of the sulphide may then be heated in an atmosphere of dry carbonic dioxide, in the usual manner. This method applies to the

greater number of cases. In its place we may often, but not always, employ the following, which usually gives good results in the cases of the alkaline salts. Potassic cyanide, as free as possible from carbonate and cyanate, is to be fused in a crucible of Berlin porcelain, and then allowed to cool. A weighed portion of the antimonoso-tungstate is then to be placed upon the fused mass, and the whole cautiously heated to low redness, and kept for a short time at this temperature. The antimony is completely reduced to metal, and after the solution of the alkaline salts in cold water, and washing at first with water and afterward with alcohol, may be weighed upon an asbestos filter. It will be seen that this process is the same as that devised many years ago by myself for the separation of tin from tungsten, worked out in my laboratory by Mr. F. H. Talbutt,\* and known as Talbutt's method. The process unfortunately does not apply to cases in which insoluble compounds are formed together with the reduced metallic antimony. As a rule, when the process is successful, the antimony is finally in the form of large bright metallic globules, but in some cases it forms on reduction wholly or partially a black powder containing tungsten, and the method then fails. In these cases an accurate result may be obtained by mixing the salt or the potassic cyanide with a quantity of potassic or sodic carbonate sufficient to completely saturate both the tungstic and antimonious oxides present. This variation in the application of the method is due to my assistant, Mr. Herman Schmidt. In determining antimonious or antimonious oxides by this process, there is, of course, the disadvantage that a higher is always estimated from a lower molecular weight. The following analyses will serve to show the degree of accuracy which may be obtained under favorable circumstances, the method applying to antimonio-tungstates as well as to the antimonoso series. In an antimonio-tungstate of potassium not of definite constitution,

1.0924 gr. gave 0.4407 gr. metallic antimony = 53.79 %  $\text{Sb}_2\text{O}_3$

1.0316 gr. " 0.4155 gr. " " = 53.71 % "

In another compound,

0.9059 gr. gave 0.2251 gr. metallic antimony = 33.13 %  $\text{Sb}_2\text{O}_3$

1.0312 gr. " 0.2558 gr. " " = 33.08 % "

Antimonious oxide may also be determined in these compounds by titration with iodine, after adding to the solution an alkaline tartrate

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\* Am. Journal of Science and Arts, I. 7.

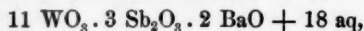
and an excess of sodic bicarbonate. It will be found advantageous to standardize the solution of iodine by means of pure crystallized antimonio-potassic tartrate, — of course, after addition of an alkaline dicarbonate.

The determination of tungstic oxide may be effected by first separating the antimony as sulphide, and then precipitating the hot solution with baric chloride, after adding ammonia in small excess. The baric tungstate may be weighed upon an asbestos filter. It is better, however, to precipitate the tungstic oxide by means of mercurous nitrate; only, in case this method is to be applied, the antimony must be precipitated as sulphide after the addition of dilute sulphuric acid, and chlorhydric acid must not be employed.

11:3 *Baric Antimonoso-tungstate*. — A solution of sodic antimonoso-tungstate, obtained as above, gives with baric chloride a heavy pale yellow curdy or indistinctly crystalline precipitate. This salt melts under hot water to a thick yellow oily liquid, which dissolves very slowly, requiring a large quantity of water for solution. The solution has a yellow color and an acid reaction. It gives pale yellow flocky precipitates, with mercurous, argentic, and thalious nitrates. Of this salt,

1.0722 gr. lost on ignition with $\text{WO}_3\text{Na}_2$	0.0858 gr. =	8.00 %
1.3057 gr. gave	0.3318 gr. $\text{Sb}_2\text{S}_3$	= 21.78 % $\text{Sb}_2\text{O}_3$
1.3668 gr. “	0.3371 gr. “	= 21.17 % “
1.2543 gr. “	0.1440 gr. $\text{SO}_4\text{Ba}$	= 7.54 % Ba O
1.4895 gr. “	0.1709 gr. “	= 7.53 % “
1.9450 gr. “	1.6599 gr. oxides ( $\text{WO}_3 + \text{Sb}_2\text{O}_3$ )	= 85.34 %

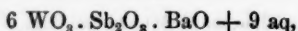
The analyses lead to the formula



which requires :

		Calc'd.		Found.	
11 $\text{WO}_3$	2552	63.07	} 84.42	62.79	62.99
3 $\text{Sb}_2\text{O}_3$	864	21.35		21.17	21.78
2 BaO	306	7.57		7.54	7.53
18 $\text{H}_2\text{O}$	324	8.00		8.00	
	4046	100.00			

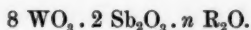
The salt may be reduced to the type



if we suppose  $\text{Sb}_2\text{O}_3$  partially to replace  $\text{WO}_3$ ; but in view of the very frequent recurrence of 22 molecules of tungstic oxide among complex inorganic acids, I am disposed to double the formula given above, and to write



In the yellow oily salt obtained by precipitating sodic antimonosotungstate by means of potassic bromide, and carefully washing with a cold strong solution of the bromide, the ratio of the tungstic to the antimonious oxide was determined and found to be nearly  $8 \text{WO}_3$  to  $2 \text{Sb}_2\text{O}_3$ , so that there is probably a series of antimonosotungstates with the general formula



The quantity of solution taken gave  $0.1091 \text{ gr. Sb}_2\text{S}_3 = 0.0935 \text{ gr. Sb}_2\text{O}_3$ , and  $0.3417 \text{ gr. WO}_3 = 71.51 \% \text{ WO}_3$  and  $21.49 \% \text{ Sb}_2\text{O}_3$ .

#### ANTIMONOSO-MOLYBDATES.

The salts of this series are readily formed by boiling antimonious oxychloride,  $\text{SbOCl}$ , with an acid molybdate. The conditions are exactly the same as in the case of the corresponding antimonosotungstates. There is almost always a greater or less reduction of the molybdic oxide, and the solutions obtained have a greenish or greenish-blue tint from the presence of  $\text{Mo}_2\text{O}_3$  or a similar oxide. The ordinary acid ammonic molybdate of commerce in cold solution readily dissolves freshly precipitated antimonious oxide with only a slight reduction of the molybdic oxide; on boiling, much reduction takes place.

*Analytical Methods.* — Antimonious oxide cannot be separated from molybdic oxide by means of hydric sulphide, as a greater or less proportion of molybdic sulphide is always found. By proceeding in the manner already pointed out for the separation of antimony from tungsten, it is possible, in many cases at least, to separate antimony from molybdenum with a very satisfactory degree of accuracy. It will be found, however, always advantageous to add a quantity of potassic or sodic carbonate sufficient to neutralize both the molybdic and antimonious oxides before fusion with potassic cyanide. Crucibles of the best Berlin porcelain are alone adapted to fusions of this kind, and even when these are employed the action of the alkaline mixture upon the crucible must be taken into account. The best method is to add

to the solution an alkaline tartrate, and then to render it alkaline with an excess of sodic bicarbonate. The antimonious oxide may then be determined by titration with iodine.

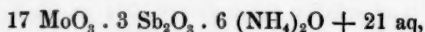
17 : 3 *Ammonic Antimonoso-molybdate*.—This salt crystallizes from a solution of antimonious oxide in 14 : 6 ammonic molybdate, in pale greenish-yellow granular crystals, but its preparation is rather uncertain. It is insoluble in cold water: for analysis, the crystals were simply washed and dried upon woollen paper. In this salt,

0.7474 gr. gave by titration with iodine 0.1618 gr.  $\text{Sb}_2\text{O}_3 = 21.65\%$

0.5287 gr. " 0.0399 gr.  $(\text{NH}_4)_2\text{O} = 7.55\%$

1.0869 gr. lost on ignition with  $\text{MoO}_4\text{Na}_2$  and  $\text{WO}_4\text{Na}_2$  0.1851 gr. = 17.03 %.

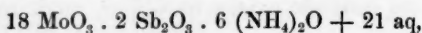
The analyses lead to the formula



which requires :

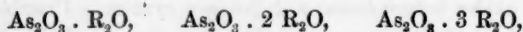
		Calc'd.	Found.
17 $\text{MoO}_3$	2448	61.18	61.32
3 $\text{Sb}_2\text{O}_3$	864	21.59	21.65
6 $(\text{NH}_4)_2\text{O}$	312	7.79	7.55
21 $\text{H}_2\text{O}$	378	9.44	9.48
	4002	100.00	

The molybdic oxide is estimated by difference. The solution from which this salt of ammonium separated gave, after twenty-four hours, a fine yellow crystalline precipitate with manganous sulphate. The formula given may be reduced to the type



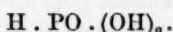
if we assume that one molecule of  $\text{Sb}_2\text{O}_3$  plays the part of, or replaces, one molecule of molybdic oxide. In determining the water in this salt I employed a mixture of equal molecules of sodic tungstate and molybdate, which fuses at a temperature below that at which molybdic oxide is given off.

In formulating the arsenoso-tungstates and arsenoso-molybdates I have assumed provisionally that normal arsenites are represented by one or another of the three general formulas

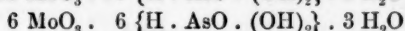
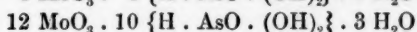
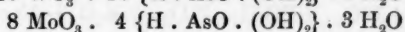
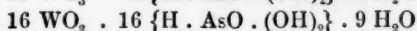
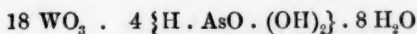


the three plumbic arsenites forming appropriate special instances. This view would establish a broad line of distinction between arsenites

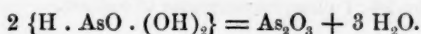
and phosphites, which last are now generally considered as hydryl-phosphinates, the general formula being



On the other hand, the existence of alkyl-arsinic acids appears to prove beyond a doubt that at least *some* arsenites belong to the same type with the phosphites. The older view must in any case be true for certain classes of salts, because the arsenites are not all reducible to the type  $\text{H} \cdot \text{AsO} \cdot (\text{OH})_2$ , even if we admit that the atom of hydrogen is replaceable by an atom of univalent metal, for which there is no sufficient evidence in the case of the phosphites. If we consider the arsenic in the arsenoso-tungstates and arsenoso-molybdates which I have described to exist in the form of hydryl-arsinic acid, we shall have for the corresponding acids, respectively, the formulas



in which, of course, the basicity is purely arbitrary, since it depends in each case upon the number of molecules of base in a single salt. The internal basicity, as measured by the hydroxyl in the arsenical term, is always two, corresponding to one in the old style of writing. As the salts described appear to give off all their water when heated without other decomposition than loss from the volatilization of arsenous oxide, it would seem to follow that their formulas must then at least be written as if they contained all the arsenic as  $\text{As}_2\text{O}_3$ , since



#### PHOSPHOROSO-PHOSPHO-TUNGSTATES.

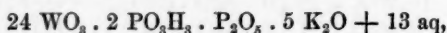
24:1:2:5 *Potassic Phosphoroso-phospho-tungstate*. — When a solution containing both phosphorous and orthophosphoric acids is added to one of 12:5 sodic tungstate, no precipitate is formed, but on adding potassic bromide a white crystalline salt is thrown down, slightly soluble in cold water, but soluble in a large quantity of boiling water, forming a turbid liquid which has an acid reaction. The solution gives no precipitate with cupric sulphate, even on boiling and with or without free chlorhydric acid. It gives a white flocky precipitate with

argentic nitrate, which becomes darker on boiling, and finally deep chocolate-brown. This reaction resembles that of the phospho-hypo-phospho-tungstates. The solution gives a very pale yellow indistinctly crystalline precipitate with mercurous nitrate, which is not reduced by boiling, and a white flocky precipitate with baric chloride. The salt dissolves with much difficulty in ammonia-water, but easily in solutions of alkaline carbonates. Chlorhydric acid gives a white precipitate in these solutions, readily soluble in ammonia. In this salt,

{ 1.5373 gr. lost on ignition	0.0578 gr.	=	3.76%	
{ 1.5373 gr. gave	1.3702 gr. mixed oxides	=	89.13%	WO <sub>3</sub> and P <sub>2</sub> O <sub>5</sub>
1.7603 gr. "	0.1138 gr. P <sub>2</sub> O <sub>7</sub> Mg <sub>2</sub>	=	4.13%	P <sub>2</sub> O <sub>5</sub>
2.7325 gr. "	0.0836 gr. "	=	1.96%	"

In determining PO<sub>3</sub>H<sub>3</sub> the solution in CO<sub>3</sub>Na<sub>2</sub> was oxidized by bromine.

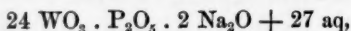
The analyses correspond with the formula



which requires:

		Calc'd.		Found.
24 WO <sub>3</sub>	5568	84.75	} 86.91	85.00
P <sub>2</sub> O <sub>5</sub>	142	2.16		1.96
2 PO <sub>3</sub> H <sub>3</sub>	164	2.49		2.50
5 K <sub>2</sub> O	472	7.18		7.11
13 H <sub>2</sub> O	224	3.41		3.43
	<hr/> 6570	<hr/> 100.00		

When a solution of phosphorous and chlorhydric acids is mixed with one of the 24 : 1 phospho-tungstate of sodium,



no precipitate is formed, but after a time relatively large colorless measurable crystals of the phospho-tungstate are deposited.

#### PHOSPHOROSO-PHOSPHO-MOLYBDATES.

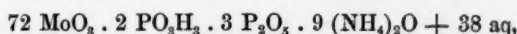
72 : 3 : 2 : 9 *Ammonic Phosphoroso-phospho-molybdate*. — When the solution of phosphorous and chlorhydric acids obtained by treating phosphorous terchloride with cold water is mixed with a solution of 10 : 2 ammonic phospho-molybdate, a greenish-yellow crystalline pre-

precipitate is thrown down at once. The salt is very insoluble in water. It was washed upon the filter-pump and dried on woollen paper for analysis. In this salt,

1.0222 gr. lost with $\text{WO}_4\text{Na}_2$	0.0975 gr. = 9.54%
0.8936 gr. gave $0.0354 \text{ gr. } (\text{NH}_4)_2\text{O}$	= 3.96%
1.1348 gr. " $0.0646 \text{ gr. } \text{P}_2\text{O}_5$	= 3.63%
1.2439 gr. " $0.0696 \text{ gr. } \text{P}_2\text{O}_5$	= 3.58%

The determination of phosphoric oxide was made after oxidation by bromine.

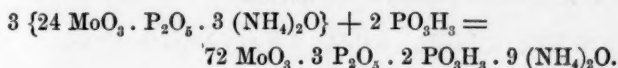
The analyses agree very well with the formula



which requires :

		Calc'd.	Found.
72 $\text{MoO}_3$	10368	85.61	85.56
3 $\text{P}_2\text{O}_5$	426	3.52	3.58 3.63
2 $\text{PO}_3\text{H}_3$	164	1.35	1.50
9 $(\text{NH}_4)_2\text{O}$	468	3.87	3.96
38 $\text{H}_2\text{O}$	684	5.65	5.58
	<hr/> 12110	<hr/> 100.00	

The formation of this salt may be represented by the equation



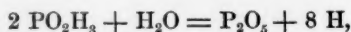
#### PHOSPHO-HYPOPHOSPHO-TUNGSTATES.

26 : 4 : 2 *Potassic Phospho-hypophospho-tungstate.* — When the 24 : 1 phospho-tungstate of sodium is boiled with an excess of a solution of hypophosphorous acid and a solution of potassic bromide is added to the clear pale blue filtrate, a white crystalline precipitate is after a time thrown down. The salt dissolves readily in hot water to a clear solution. This gives a white flocky crystalline precipitate with baric chloride, a pale yellow precipitate with mercurous nitrate, and a white precipitate with argentic nitrate, which on boiling becomes first yellow, then brown, and finally takes a brownish color, and deposits a precipitate closely resembling ferric hydrate. Cuprous sulphate is without action on the solution. For analysis the freshly formed salt

was thrown upon a filter, washed on the filter-pump thoroughly with cold water, and finally dried for analysis upon woollen paper. Of this preparation,

1.2162 gr.	gave 0.9706 gr. mixed oxides	= 79.81%
1.9865 gr.	" 1.5903 gr. "	= 80.05%
1.0921 gr.	" 0.1408 gr. $P_2O_7Mg_2$	= 8.25% $P_2O_5$
1.5059 gr.	" 0.1552 gr. "	= 6.59% "
1.2162 gr.	" 0.6340 gr. $PtCl_6K_2$	= 10.12% $K_2O$
0.9633 gr.	" 0.5074 gr. "	= 10.22% "
1.2705 gr.	lost with $WO_4Na_2$ 0.1138 gr.	= 8.96%
0.8472 gr.	" " " 0.0778 gr.	= 9.18%

In the analyses the hypophosphorous acid was determined by oxidation with bromine, after adding an excess of sodic carbonate. The total phosphoric acid was then determined as ammonio-magnesian phosphate. In another portion of the salt the phosphoric acid proper was precipitated directly by magnesia-mixture in the usual manner. Corrections are of course made for the loss of hydrogen in ignition, according to the equation

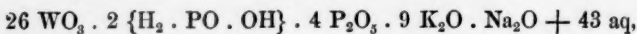


and also for the retention of one atom of oxygen by the mixed oxides, as shown by the same equation.

The analyses correspond to the formula



or,



which requires :

		Calc'd.	Found.	
26 $WO_3$	6032	71.66	71.56	71.80
4 $P_2O_5$	568	6.74	6.59	
2 $PO_2H_3$	132	1.57	1.55	
9 $K_2O$	850	10.09	10.12	10.22
$Na_2O$	62	0.74	0.78	(diff.)
43 $H_2O$	774	9.20	9.23	
	<hr/> 8418	<hr/> 100.00		

It cannot be doubted that similar compounds containing molybdenum in place of tungsten remain to be discovered. I did not, how-

ever, succeed in obtaining them by the action of hypophosphorous acid upon phospho-molybdates, and the precise conditions necessary are yet to be determined. It appears to be at least probable that classes of phosphoroso-hypophospho-tungstates and phosphoroso-hypophospho-molybdates will sooner or later be discovered.

#### ARSENOSO-PHOSPHO-TUNGSTATES.

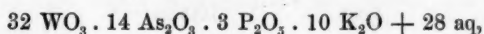
The salts of this series are formed when solutions of orthophosphates and arsenoso-tungstates are mixed, and when arsenous oxide is boiled with a solution of an alkaline phospho-tungstate. The alkaline salts are sometimes crystalline and sometimes gummy. The series is probably a very extensive one.

*Analytical Methods.* — In these salts the arsenous oxide is best determined by titration with iodine after adding an excess of an alkaline dicarbonate. After separating arsenous oxide as sulphide by sulphydric acid, the phosphoric oxide may be determined by magnesia-mixture. Phosphoric and tungstic oxides may be determined together by mercurous nitrate and mercuric oxide after separating arsenous oxide from the solution as arsenous sulphide, dilute sulphuric acid being employed in place of chlorhydric acid. Water is best determined by heating over a radiator.

32 : 14 : 3 : 10 *Potassic Arsenoso-phospho-tungstate.* — This salt was prepared by boiling potassic phospho-tungstate with an excess of finely pulverized arsenous oxide. The filtered solution had a pale greenish-yellow tint, and after standing twenty-four hours deposited a mass of very minute greenish-yellow crystals. These were filtered off, washed with cold water, and then drained by the filter-pump. The drained mass was greenish yellow, and packed into a gummy solid. The filtrate on evaporation gave a fresh quantity of the same salt, which is rather soluble in cold, and very easily soluble in hot water. Of this salt,

0.9333 gr. lost by heating over a radiator	0.0398 gr. =	4.27%
0.9333 gr. gave	0.6094 gr. $\text{WO}_3 + \text{P}_2\text{O}_5$	= 65.29%
1.0505 gr. “	0.2413 gr. $\text{As}_2\text{O}_3$ with iodine	= 22.97%
0.8456 gr. “	0.0472 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 3.57%

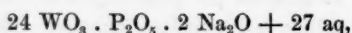
The analyses correspond fairly well with the formula



which requires :

		Calc'd.	Found.
32 $\text{WO}_3$	7424	61.51	61.72
14 $\text{As}_2\text{O}_3$	2772	22.96	22.97
3 $\text{P}_2\text{O}_5$	426	3.53	3.57
10 $\text{K}_2\text{O}$	944	7.82	7.58
28 $\text{H}_2\text{O}$	504	4.18	4.27
	<hr/> 12070	<hr/> 100.00	

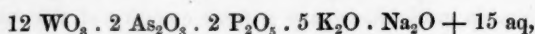
12 : 2 : 2 : 6 *Sodio-potassic Arsenoso-phospho-tungstate*. — When sodic phospho-tungstate,



in solution, is boiled with arsenous oxide in excess, this last dissolves freely to a colorless or nearly colorless liquid. On adding ammoniac chloride no precipitate is formed, but after acidulating with chlorhydric acid a white crystalline precipitate is thrown down. On standing, the supernatant liquid deposits very distinct pale yellow tabular crystals. When potassic bromide is added to the sodic solution, a yellow oil separates after a time, which dries to a pale yellow gummy transparent mass. Of this salt,

0.9284 gr. lost over a radiator	0.0595 gr.	=	6.41%
0.9492 gr. gave	0.0822 gr. $\text{As}_2\text{O}_3$ with iodine	=	8.65%
1.2191 gr. “	0.1061 gr. “ “	=	8.70%
0.8961 gr. “	0.0944 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	=	6.74% $\text{P}_2\text{O}_5$
{ 0.8916 gr. “	0.6458 gr. $\text{P}_2\text{O}_5 + \text{WO}_3$	=	72.43%
{ 0.8916 gr. “	0.5064 gr. $\text{PtCl}_6\text{K}_2$	=	11.03% $\text{K}_2\text{O}$

The formula which best represents the analyses is



which requires :

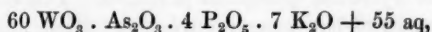
		Calc'd.	Found.
12 $\text{WO}_3$	2784	65.24	65.69
2 $\text{As}_2\text{O}_3$	396	9.28	8.65
2 $\text{P}_2\text{O}_5$	284	6.65	6.74
5 $\text{K}_2\text{O}$	472	11.06	11.03
$\text{Na}_2\text{O}$	62	1.45	1.48
15 $\text{H}_2\text{O}$	270	6.32	6.41
	<hr/> 4268	<hr/> 100.00	

The arsenous oxide is too low, but the sum of the arsenous and tungstic oxides, as well as the percentages of the other constituents of the salts, agree well with the formula.

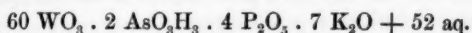
60 : 1 : 4 : 7 *Potassic Arsenoso-phospho-tungstate*. — When a solution of potassic phosphate is poured into one of sodic arsenoso-tungstate as prepared by boiling arsenous oxide with 12 : 5 sodic tungstate, no precipitate is formed; but on adding chlorhydric acid the liquid becomes yellow, and, after standing, deposits beautiful pale yellow crystals. For analysis these were washed with cold water and dried on woollen paper. The salt is soluble in hot water, but appears to be decomposed by solution. In this salt,

1.2498 gr. gave 0.0671 gr. $P_2O_7Mg_2$	= 3.43% $P_2O_5$
1.2587 gr. " 0.0151 gr. $As_2O_3$ by iodine	= 1.20%
1.0348 gr. " 0.9192 gr. $WO_3 + P_2O_5$	= 88.81%
1.3143 gr. lost over a radiator 0.0787 gr.	= 5.99% water.

The analyses correspond closely to the formula



which may also be written



The formula requires:

		Calc'd.	Found.
60 $WO_3$	13920	85.21	85.38
4 $P_2O_5$	568	3.48	3.43
$As_2O_3$	198	1.21	1.20
7 $K_2O$	661	4.04	4.00 (diff.)
55 $H_2O$	990	6.06	5.99
	<hr/> 16337	<hr/> 100.00	

It is of course very possible that this may be a double salt, but there are at present no data upon which we can base a rational distribution of the components.

#### ARSENOSO-ARSENIO-TUNGSTATES.

The salts which belong to this group are formed under the same conditions as the corresponding arsenoso-phospho-tungstates. They are in many cases highly crystalline and well defined, and appear to be very numerous.

*Analytical Methods.* — Arsenic acid may be directly determined in the soluble salts of this series by means of magnesia-mixture, but it is best to redissolve the precipitated ammonio-magnesian arsenate in chlorhydric acid, and precipitate a second time by ammonia. Arsenous oxide may be determined by titration with iodine after adding an excess of an alkaline dicarbonate. As a check upon the determination of the two oxides of arsenic, it is well to oxidize a portion of the salt directly by means of nitric acid, and then determine the total arsenic oxide by means of magnesia-mixture. A further check may also be obtained by reducing the arsenic oxide by boiling with sulphurous acid, and then titrating the total arsenous oxide by means of iodine. In solutions from which the arsenic has been completely removed as  $\text{As}_2\text{S}_3$ , tungsten can be determined by means of mercurous nitrate, provided that no chlorhydric acid or chloride is present.

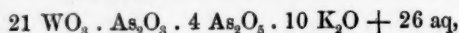
21 : 1 : 4 : 10 *Potassic Arsenoso-phospho-tungstate.* — When potassic bromide is added to a solution of arsenoso-tungstate of soda, and a solution of potassic arsenate,  $\text{AsO}_4\text{K}_2\text{H}$ , is then poured into the clear filtrate, a white crystalline precipitate is formed. This salt requires a very large quantity of hot water for solution. Baric chloride boiled with it gives a well-defined flocky-crystalline salt. Argentic nitrate gives a similar salt, but this has a faint tinge of fawn-color, perhaps due to the presence of a trace of potassic arsenate not completely removed by washing. Mercurous nitrate gives on boiling a clear yellow flocky-crystalline salt. In the potassic salt,

1.9985 gr. gave 0.3468 gr.  $\text{As}_2\text{O}_7\text{Mg}_2$  = 12.36%  $\text{As}_2\text{O}_5$   
 2.0085 gr. “ 0.0527 gr.  $\text{As}_2\text{O}_5$  by iodine = 2.62%  $\text{As}_2\text{O}_5$

After complete oxidation by nitric acid,

1.5004 gr. gave 0.3162 gr.  $\text{As}_2\text{O}_7\text{Mg}_2$  = 15.63%  $\text{As}_2\text{O}_5$   
 1.9684 gr. “ 1.2935 gr.  $\text{WO}_3$  = 65.72%  
 1.5825 gr. “ 1.0346 gr. “ = 65.37%  
 1.3890 gr. “ 0.9382 gr.  $\text{PtCl}_6\text{K}_2$  = 13.09%  $\text{K}_2\text{O}$   
 1.5765 gr. lost over a radiator 0.0955 gr. = 6.06%

The analyses lead to the formula



which requires :

		Calc'd.	Found.	
21 $\text{WO}_3$	4872	65.86	65.72	65.37
As <sub>2</sub> O <sub>3</sub>	198	2.68		2.62
4 $\text{P}_2\text{O}_3$	920	12.43		12.36
10 $\text{K}_2\text{O}$	940	12.70		13.09
26 $\text{H}_2\text{O}$	468	6.33	6.06	6.39 (diff.)
	7398	100.00		

Of course, in this salt, as in the arsenoso-phospho-tungstates described, arsenic may be supposed to be in the form of  $\{\text{H} \cdot \text{AsO} \cdot (\text{OH})_2\}$  either wholly or partially.

Classes of antimonoso - arsenio - tungstates, antimonoso - antimonio-tungstates, and arsenoso-antimonio-tungstates, appear also to exist and to be formed by processes exactly analogous to those described in the cases of the compounds containing two oxides respectively of the forms  $\text{R}_2\text{O}_3$  and  $\text{R}'_2\text{O}_3$ , united with tungstic oxide.

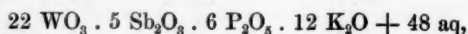
#### ANTIMONOSO-PHOSPHO-TUNGSTATES.

These salts are formed under the same conditions as the corresponding arsenoso-phospho-tungstates, and the methods of analysis to be employed are the same.

22 : 6 : 5 : 12 *Potassic Antimonoso-phospho-tungstate*. — When a solution of potassic phosphate is poured into a hot solution of sodic antimonoso-tungstate as obtained by dissolving  $\text{SbOCl}$  in 10 : 4 sodic tungstate, a very pale yellow highly crystalline salt is at once formed. This is nearly insoluble in both hot and cold water. The portion analyzed was filtered off, washed upon the filter-pump with cold water, drained, and dried upon woollen paper. The salt, like many others which I have described, could not be recrystallized, but I give the results of the analyses for what they may prove to be worth. They certainly, I think, establish the existence of the series. In this salt,

{ 0.7776 gr. gave 0.6142 gr. oxides	= 78.99%
{ 0.7776 gr. " 0.4763 gr. $\text{PtCl}_5\text{K}_2$	= 11.90%
1.0323 gr. " with iodine 0.1594 gr. $\text{Sb}_2\text{O}_3$	= 15.44%
0.9716 gr. " " 0.1509 gr. "	= 15.53%
1.2300 gr. " 0.1805 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 9.20% $\text{P}_2\text{O}_3$
1.2430 gr. " 0.1821 gr. "	= 9.37% "

The analyses lead to the formula:



which requires:

		Calc'd.	Found.	
22 $\text{WO}_3$	5104	54.34	54.23	
6 $\text{P}_2\text{O}_5$	852	9.07	9.20	9.37
5 $\text{Sb}_2\text{O}_3$	1440	15.33	15.44	15.53
12 $\text{K}_2\text{O}$	1133	12.07	11.90	
48 $\text{H}_2\text{O}$	864	9.19	9.13 (diff.)	
	<hr/> 9393	<hr/> 100.00		

#### ANTIMONIO-TUNGSTATES.

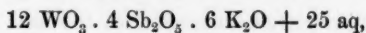
As already stated, these compounds are formed by the direct oxidation of antimonoso-tungstates, one molecule of oxygen being absorbed. I shall hereafter show that, in place of oxygen, platinous chloride and other divalent compounds may serve as complex replacing molecules. Antimonio-tungstates are also formed when antimonie hydrate in excess is boiled with an acid tungstate, and when tungstic teroxide is digested or boiled with an alkaline antimonate. The salts of this series are, as a whole, not so well defined as the phospho-tungstates, vanadio-tungstates, and arsenio-tungstates, and are much more difficult to prepare in a state of purity.

*Analytical Methods.* — These are essentially the same as those which I have given in the case of the antimonoso-tungstates. Antimonie and tungstic oxides may be precipitated together by mercurous nitrate and mercuric oxide. In the ignited precipitate it must be assumed that the antimony is in the form of tetroxide,  $\text{Sb}_2\text{O}_4$ , and the proper correction applied, after a special determination of the antimony, as sulphide or as metal.

*6:2 Antimonio-tungstate of Potassium.* — This salt was prepared by boiling potassic di-antimonate for a long time with a solution of 12:5 acid potassic tungstate. After filtration from a small quantity of the antimonate in excess, the filtrate, on standing twenty-four hours, deposited colorless granular crystals, which were washed with cold water and dried upon woollen paper. The salt was not very soluble in water: the crystals were soft and packed together between the fingers. In this salt,

1.0881 gr. lost on ignition with $\text{WO}_3\text{Na}_2$	0.1076 gr. =	9.89 %
1.3566 gr. " " "	0.1379 gr. =	10.16 %
1.4636 gr. gave 1.1178 gr. $\text{WO}_3 + \text{Sb}_2\text{O}_3$		= 76.36 %
1.3425 gr. " with $\text{KCy}$ 0.2529 gr. $\text{Sb}$		= 25.12 % $\text{Sb}_2\text{O}_3$
0.9095 gr. " " 0.1700 gr. $\text{Sb}$		= 24.92 % "
0.8710 gr. " 0.5011 gr. $\text{PtCl}_5\text{K}_2$		= 11.16 % $\text{K}_2\text{O}$

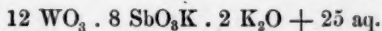
The analyses lead to the formula



which requires:

		Calc'd.	Found.	
12 $\text{WO}_3$	2784	54.81	55.04	
4 $\text{Sb}_2\text{O}_3$	1280	25.19	25.12	24.92
6 $\text{K}_2\text{O}$	566	11.14	11.16	
25 $\text{H}_2\text{O}$	450	8.86	8.91	8.64
	5080	100.00		

In calculating the results of the analysis for comparison, I have assumed that, in the ignition with the sodic tungstate to determine the water, antimonious oxide is reduced to the tetroxide  $\text{Sb}_2\text{O}_4$ ; a correction must therefore be applied to the apparent loss. This amounts to one twentieth of the percentage of antimonious pentoxide, and is of course to be deducted from the total loss. Chemists usually admit the existence of three classes of antimonates, corresponding respectively to metaphosphates, pyrophosphates, and orthophosphates, and formulas to support this view have been somewhat arbitrarily assigned to known compounds. If we suppose that the antimonio-tungstate above described contains metantimonious oxide, we may write the formula as we shall write those of corresponding metaphospho-tungstates,



A solution of this salt gives white crystalline precipitates with baric chloride, argentic nitrate, and cupric sulphate, and a yellow floccy-crystalline precipitate with mercurous nitrate.

#### ANTIMONIO-MOLYBDATES.

Salts belonging to this group are formed when freshly prepared antimonious hydrate is boiled with an acid molybdate in solution, when antimonious pentachloride in solution in chlorhydric acid is poured into a solution of an alkaline molybdate in small quantities at a time,

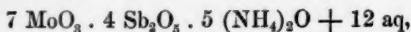
and when molybdic oxide is digested with a solution of an alkaline antimonate.

*Analytical Methods.*—The separation of animony from molybdenum cannot be effected by sulphydric acid, because molybdic sulphide is always precipitated in greater or less quantity, even when phosphoric acid is present in the solution. The only method which I have been able to devise consists in fusing the salt to be analyzed or the mixture of oxides with potassic cyanide, as in the case of the separation of antimony from tungsten. In this case also it is always advisable, and sometimes necessary, to add a sufficient quantity of an alkaline carbonate to form a mixture of neutral molybdate and antimonate, as suggested by Mr. Herman Schmidt. With proper care the two oxides may be precipitated together by mercurous nitrate and mercuric oxide, and ignited without sensible loss of molybdic oxide; but there is then always a certain amount of reduced metallic antimony present, and on the whole the method is not to be recommended.

*7:3:5 Ammonic Antimonio-molybdate.*—Antimonic hydrate dissolves readily on boiling with a strong solution of 14:6 ammonic molybdate. The hydrate should be in excess, and should be added in small portions at a time, until, after long boiling, a part remains undissolved. After standing twenty-four hours, beautiful colorless crystals are deposited in quantity. These have a nacreous lustre, and are readily soluble in hot water. In this salt,

1.0647 gr. lost on ignition with  $\text{WO}_4\text{Na}_2$  0.2052 gr. = 19.55 %  
 1.2234 gr. gave 0.2418 gr.  $\text{NH}_4\text{Cl}$  = 9.60 %  $(\text{NH}_4)_2\text{O}$   
 0.9576 gr. “ with  $\text{KCy}$  0.3321 gr.  $\text{Sb}$  = 46.24 %  $\text{Sb}_2\text{O}_5$ .

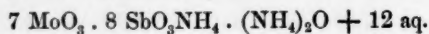
The analyses correspond with the formula



which requires :

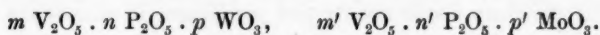
		Calc'd.	Found.
7 $\text{MoO}_3$	1008	36.47	36.52
4 $\text{Sb}_2\text{O}_5$	1280	46.31	46.24
5 $(\text{NH}_4)_2\text{O}$	260	9.40	9.60
12 $\text{H}_2\text{O}$	216	7.82	7.64
	<hr/> 2764	<hr/> 100.00	

The formula may also be written

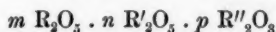


The solution of this salt gives with manganeous sulphate after a time a fine canary-yellow crystalline precipitate. The ammonium salt appears to be decomposed by evaporation to dryness, or perhaps by the act of solution. The dry residue, on addition of water, leaves a white insoluble crystalline substance.

The existence of classes of vanadio-phospho-tungstates and vanadio-phospho-molybdates has already been proved. These may be embraced under the general formulas



I believe that I am fully justified, though from qualitative experiments only, in maintaining that the formula



is general, and that  $\text{R}_2\text{O}_5$  and  $\text{R}'_2\text{O}_5$  may represent any two pentoxides, at least of the series  $\text{P}_2\text{O}_5 \cdot \text{V}_2\text{O}_5 \cdot \text{As}_2\text{O}_5$  and  $\text{Sb}_2\text{O}_5$ .

#### PYROPHOSPHO-TUNGSTATES.

The phospho-tungstates and phospho-molybdates which have hitherto been described must be regarded as containing phosphoric oxide in the modification in which it exists in the class of tribasic or ortho phosphates. This appears to be clearly shown, first, by the synthesis of these compounds from orthophosphoric acid and orthophosphates and the acid tungstates and molybdates; and, secondly, from the fact that in all cases, after the addition of an excess of ammonia, magnesia-mixture at once throws down the characteristic ammonio-magnesian orthophosphate. I shall now show that the other modifications of phosphoric oxide or acid enter as such into similar compounds, so that we have perfectly well defined groups of pyrophospho-tungstates, metaphospho-tungstates, etc., and corresponding compounds containing molybdenum; and that, in the compounds so formed, the various modifications of phosphoric oxide preserve as it were their individuality. I shall further render it at least probable that there are groups — of phospho-tungstates for instance — in which two different modifications of phosphoric oxide may exist, each preserving its own characteristic properties. I do not now assert that in each of the complex groups which I have described orthophosphoric acid may be replaced by some other modification. That remains for experimental investigation. It is at least clear that the field already opened for study is one of

practically unlimited extent, as even an elementary application of the algebraical theory of permutations and combinations will show.

*Pyrophospho-tungstates* are formed when tungstic hydrate or tungstic oxide which has not been ignited is boiled with an alkaline pyrophosphate. The oxide readily dissolves, usually forming a yellow liquid. It is best to employ sodic pyrophosphate, as this gives a much more soluble salt, but the pyrophosphate must be specially prepared in the laboratory, and the tungstic oxide should be in excess. Neutral salts of the heavy metals usually give precipitates in solutions of the alkaline pyrophospho-tungstates; these precipitates are not necessarily salts of the same group, but are very often at least either pyrophosphates of the metallic bases or double pyrophosphates of the metal and of sodium or potassium.

*Analytical Methods.* — These are the same as those which I have employed in the case of the orthophospho-tungstates, only in the determination of the phosphoric oxide it is necessary to evaporate the salt two or three times in succession to dryness with an excess of chlorhydric acid, so as to convert the phosphoric acid present completely into the ortho or tribasic form. In the absence of any standard of comparison, it is necessary to speak with much hesitation, but it has always appeared to me that in these salts — in other words, in the presence of tungstic oxide — the conversion of pyrophosphoric acid into orthophosphoric acid is more difficult, or at least takes place more slowly, than in the case of the ordinary pyrophosphates. Tungstic and phosphoric oxides may in these compounds also be precipitated together by mercurous nitrate and mercuric oxide.

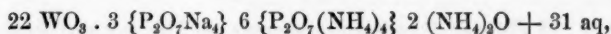
22:3:6 *Ammonio-sodic Pyrophospho-tungstate.* — A boiling solution of sodic pyrophosphate readily dissolves tungstic oxide as prepared by the action of chlorhydric or nitric acid upon calcic tungstate, but not ignited. The filtrate has a dull yellow color, and gives with a strong solution of ammonic chloride an abundant white crystalline precipitate, which cannot be purified by recrystallization, but which may be well washed upon the filter-pump with cold water, in which it is soluble to a very small extent. Hot water in large excess dissolves it, but even cold ammonia water dissolves it with much difficulty. When boiled for a long time with a solution of mercurous nitrate, the salt gives at first a white and finally a yellow mercurous salt. Argentic nitrate in solution gives at first with the salt extremely minute talcose scales, but on boiling for some time the whole dissolves to a clear liquid. When the salt is boiled with a solution of baric chloride, a flocky-crystalline white baric salt is formed. Cupric sulphate on boil-

ing dissolves the pyrophospho-tungstate, but on cooling a pale green crystalline body separates, which does not contain tungsten. The salt, precipitated by ammoniac chloride as above, after washing with cold water and drying upon woollen paper, was analyzed :

0.6626 gr. lost on ignition	0.1060 gr. = 16.00 NH <sub>3</sub> and H <sub>2</sub> O
0.9866 gr. gave	0.2479 gr. P <sub>2</sub> O <sub>7</sub> Mg <sub>2</sub> = 16.07 % P <sub>2</sub> O <sub>5</sub>
0.5488 gr. " "	0.0499 gr. (NH <sub>4</sub> ) <sub>2</sub> O = 9.09 %
0.8188 gr. " "	0.6504 gr. oxides = 79.46 % WO <sub>3</sub> and P <sub>2</sub> O <sub>5</sub> .

In determining the phosphoric oxide, the salt was several times in succession evaporated to dryness with nitric acid.

The analyses agree with the formula



which requires :

		Calc'd.	Found.
22 WO <sub>3</sub>	5104	63.48	63.39
9 P <sub>2</sub> O <sub>5</sub>	1278	15.90	16.07
6 Na <sub>2</sub> O	372	4.63	4.54 (diff.)
14 (NH <sub>4</sub> ) <sub>2</sub> O	728	9.06	9.09
31 H <sub>2</sub> O	558	6.93	6.91
	<hr/> 8040	<hr/> 100.00	

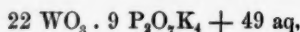
As already stated, the salt is dissolved by a large excess of hot water to a clear colorless solution. Cupric sulphate gives in this solution a pale blue crystalline precipitate of a pyrophosphate free from tungstic oxide. Argentic nitrate and baric chloride give white flocky-crystalline precipitates. Either, therefore, the salt is decomposed by solution or by the action of cupric sulphate.

22:9:18 *Potassic Pyrophospho-tungstate*. — When potassic bromide and acetic acid are added to the saturated solution of tungstic oxide in sodic pyrophosphate, a white granular fine-grained crystalline precipitate very slightly soluble in cold water is formed at once. For analysis the salt was washed upon the filter-pump with cold water, and dried on woollen paper. In this salt,

0.9440 gr. gave	0.6717 gr. oxides	= 71.15 % WO <sub>3</sub> and P <sub>2</sub> O <sub>5</sub>
1.3647 gr. " "	0.9721 gr. " "	= 71.23 % " "
0.9070 gr. " "	0.2015 gr. P <sub>2</sub> O <sub>7</sub> Mg <sub>2</sub>	= 14.21 % P <sub>2</sub> O <sub>5</sub>
0.9817 gr. lost	0.0960 gr. H <sub>2</sub> O	= 9.78 %

The phosphoric oxide was determined as before by evaporation with nitric acid to convert the pyrophosphoric into orthophosphoric acid.

The analyses correspond to the formula



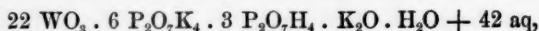
which requires:

		Calc'd.	Found.
22 $\text{WO}_3$	5104	56.94	56.94 57.02
9 $\text{P}_2\text{O}_5$	1278	14.26	14.21
18 $\text{K}_2\text{O}$	1699	18.96	19.07
49 $\text{H}_2\text{O}$	882	9.84	9.78
	<hr/> 8963	<hr/> 100.00	

22 : 9 : 13 *Potassic Pyrophospho-tungstate*. — This salt was obtained by boiling tungstic oxide for some time with potassic pyrophosphate. After filtration and standing a white crystalline salt separated, which was well drained on the filter-pump, and then washed with cold water in which it is but slightly soluble. In much boiling water it dissolves on boiling to a clear liquid. The solution gives a white crystalline precipitate with argentic nitrate, — no precipitate at first with cupric sulphate. On boiling, a very pale blue crystalline salt separates, which does not contain tungsten, and is either a cupric pyrophosphate or a double salt of potassium and copper. The solution of the pyrophospho-tungstate gives a dense white distinctly crystalline precipitate with mercurous nitrate, and a turbid solution with baric chloride yielding on boiling a white feathery crystalline salt. No precipitate is formed with manganous sulphate, but after a short time the solution becomes turbid. In this salt,

1.6112 gr. gave 1.2119 gr. oxides	= 75.22%
1.9796 gr. " 1.4894 gr. "	= 75.23%
1.6421 gr. " 0.3862 gr. $\text{P}_2\text{O}_7\text{Mg}_2$	= 15.06%
1.2433 gr. lost by direct ignition 0.1299 gr.	= 10.45%

The analyses agree closely with the formula



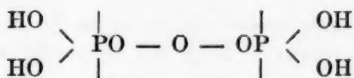
so that the type is, as in other cases,



The formula requires:

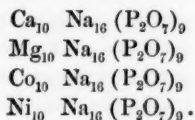
		Calc'd.	Found.
22 WO <sub>3</sub>	5104	60.11	60.17 60.18
9 P <sub>2</sub> O <sub>5</sub>	1278	15.05	15.05
13 K <sub>2</sub> O	1227	14.45	14.32 (diff.)
49 H <sub>2</sub> O	882	10.39	10.45
	<u>8491</u>	<u>100.00</u>	

All the compounds of this group which I have obtained belong, as will be seen, to the same type which contains the frequently recurring chemical mass of twenty-two molecules of tungstic oxide, united to nine molecules of pyrophosphoric acid or a pyrophosphate, together with a certain amount of base over and above that required to saturate the phosphoric oxide. We may represent this group provisionally by a structural formula containing *nine* groups of the form :



Further investigation will doubtless show that there are other series of pyrophospho-tungstates and analogous pyrophospho-molybdates. It is especially desirable to study the compounds which remain in solution after the precipitation of part of the pyrophosphoric oxide by means of cupric sulphate.

It may here be remarked, that Wallroth \* has described a series of pyrophosphates which contain *nine* molecules of P<sub>2</sub>O<sub>7</sub>, united in each case to thirty-six atoms of metal. Thus we have



It would therefore appear that similar complex molecules enter directly into combination with twenty-two molecules of tungstic oxide, but that the complexity is not necessarily due to a determining action on the part of the latter.

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\* Bull. de la Soc. Chimique, [2,] xxxix. 816.

## MONOMETAPHOSPHO-TUNGSTATES.

In preparing the salts of this series I have employed ordinary glacial phosphoric acid, which, according to Brescius,\* contains about 50% of sodic metaphosphate, and which may be regarded as a mixture of sodic metaphosphate and metaphosphoric acid. I have assumed that the acid is here in the form of monometaphosphoric acid, although upon this point the evidence is still insufficient. As the relations of metaphosphoric acid to indicators of various kinds have not hitherto been studied, the following brief note may be of interest. A solution of glacial phosphoric acid is neutral to tropæolin. The same solution required for equal volumes with purpurin 23 cc. sodic hydrate solution; with hæmatoxylin, 14 cc.; and with alizarin, 12.5 cc. No definite end reaction could be obtained with phenol-phthalein, methyl-orange, or rosolic acid.

Monometaphospho-tungstates are formed by the direct action of the acid upon acid tungstates. They are, frequently at least, gummy uncrystalline bodies. When crystalline the crystals are usually soft, and pack together readily. The salts of the alkaline earths are usually more or less distinctly crystalline. Those of the heavy metallic oxides are often pasty, and sometimes oily. They are not very readily converted into orthophospho-tungstates, and in this respect they seem to differ materially from the corresponding metaphospho-molybdates.

*Analytical Methods.* — In these salts tungstic and metaphosphoric oxides may be precipitated together by mercurous nitrate and mercuric oxide. Metaphosphoric acid may be converted into orthophosphoric acid by dissolving the salt in the least possible quantity of water, adding strong sulphuric acid, evaporating the solution nearly to dryness, and repeating this process several times. This method is very much better than fusion with alkaline carbonates, which effects the transformation of metaphosphoric acid in a very imperfect manner. I believe that I can assert with entire confidence, that in the class of monometaphospho-tungstates the conversion of the metaphosphoric into orthophosphoric acid is much more difficult than in the metaphosphates. The precipitation of the orthophosphoric acid by magnesia-mixture must of course be repeated twice.

*24:2:3 Potassic Monometaphospho-tungstate.* — When a cold freshly prepared solution of glacial phosphoric acid is digested with 10:4 potassic tungstate, part of this salt dissolves, while the undissolved

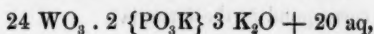
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\* Zeitschrift für analytische Chemie, vi. 187.

portion changes its character, and is converted into a soft crystalline, very slightly soluble mass. This may be filtered off, and washed with cold water. In this salt,

{ 1.5236 gr. lost on ignition	0.0857 gr. = 5.63%
{ 1.5236 gr. gave 0.0517 gr. $P_2O_7Mg_2$	= 1.96% $P_2O_5$
0.9934 gr. " 0.0303 gr. "	= 2.17% "
1.0686 gr. " 0.0352 gr. "	= 2.11% "
{ 1.1490 gr. " 1.0171 gr. oxides	= 88.52%
{ 1.1490 gr. " 0.3327 gr. $PtCl_6K_2$	= 5.70% $K_2O$

The analyses correspond very well to the formula



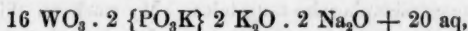
which requires:

		Calc'd.		Found.
24 $WO_3$	5568	86.36		86.38
$P_2O_5$	142	2.21	2.11	2.17 1.96
4 $K_2O$	376	5.84	5.70	5.85 (diff.)
20 $H_2O$	360	5.59		5.63
	6446	100.00		

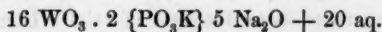
The filtrate from the 24 : 2 salt, on standing, deposits a white crystalline salt, which, when thrown on a filter and washed with cold water, presents a colorless gummy mass. Of this salt,

0.6183 gr. gave 0.0307 gr. $P_2O_7Mg_3$	= 3.17% $P_2O_5$
{ 0.8173 gr. " 0.6844 gr. oxides	= 83.72%
{ 0.8173 gr. lost on ignition 0.0607 gr.	= 7.43%

From an oversight, the potassic oxide was not determined in this salt, which may be either



or



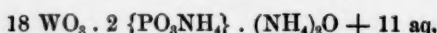
The formulas require, respectively,

		Calc'd.		Found.	Calc'd.				
16 $WO_3$	3712	80.34		80.56	80.38	3712	16 $WO_3$		
$P_2O_5$	142	3.07		3.17	3.07	142	$P_2O_5$		
3 $K_2O$	283	6.12	} 8.80	8.87	2.04	} 8.76	94	$K_2O$	
2 $Na_2O$	124	2.68					310	5 $Na_2O$	
20 $H_2O$	360	7.79		7.40	7.79		360	20 $H_2O$	
	4621	100.00			100.00		4618		

18 : 1 : 2 *Ammonic Monometaphospho-tungstate*. — When 12 : 5 ammoniac tungstate is boiled with a solution of glacial phosphoric acid, a white crystalline mass remains undissolved, very different in appearance from the ammoniac tungstate employed. This salt requires a large quantity of boiling water for solution, but is only slightly soluble in cold water. For analysis, it was thoroughly drained upon the filter-pump, and then washed with cold water. Of this salt,

1.6896 gr. lost by ignition with $\text{WO}_4\text{Na}_2$	0.1082 gr. = 6.40%
1.5026 gr. gave 0.0745 gr. $\text{P}_2\text{O}_5$	$\text{Mg}_2$ = 3.17% $\text{P}_2\text{O}_5$
1.4267 gr. “ 0.0316 gr. $(\text{NH}_4)_2\text{O}$	= 2.21%

The analyses correspond to the formula



which requires:

		Calc'd.	Found.
18 $\text{WO}_3$	4176	90.39	90.43
$\text{P}_2\text{O}_5$	142	3.08	3.17
2 $(\text{NH}_4)_2\text{O}$	104	2.25	2.21
11 $\text{H}_2\text{O}$	198	4.28	4.19
	4620	100.00	

The filtrate from this salt gives on evaporation a thick colorless syrup, in which white crystals — perhaps of the salt above described — were suspended. It will be seen that the action of  $\text{PO}_3\text{H}$  upon 12 : 5 ammoniac tungstate is essentially the same as upon the 10 : 4 potassic salt, and that in each case at least one crystalline and one gummy salt are formed.

The analyses given are sufficient to establish the existence of three classes of monometaphospho-tungstates. My work on this subject is to be regarded merely as preliminary, and is intended to direct the attention of other chemists to this class of salts. In another paper I shall give the results of a more detailed study of the various metaphospho-tungstates. Fleitmann and Henneberg have described five series of metaphosphates; in addition to these, there remain to be studied, in their relation to tungstic and molybdic oxides, the two series of tetraphosphates,  $\text{P}_4\text{O}_7 \cdot 6 \text{RO}$ , and dekaphosphates,  $\text{P}_{10}\text{O}_{19} \cdot 12 \text{RO}$ , discovered by the same chemists, as well as the new group of salts described by Salzer,\* which may be called hypophosphates.

\* Pharmaceutische Zeitung, Bunzlau, 1881. Ann. der Chemie, ccxi. 1.

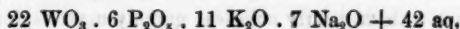
## ORTHOMETAPHOSPHO-TUNGSTATES.

A single salt of this series will be sufficient to establish the existence of compounds into which two different modifications of phosphoric acid enter, to a certain extent at least preserving their peculiar characteristics.

22 : 6 : 11 : 7 *Potassio-sodic Orthometaphospho-tungstate*. — When 24 : 1 sodic phospho-tungstate is boiled with a solution of sodic monometaphosphate,  $\text{PO}_3\text{Na}$ , the salt dissolves readily to a clear liquid. Potassic bromide gives a white precipitate in this solution. After filtering and washing with cold water, a white gelatinous mass remains upon the filter, but slightly soluble in water. Of this salt,

1.2008 gr. gave	0.8728 gr. oxides	= 72.68%
1.5959 gr. "	0.1611 gr. "	= 72.76%
1.3558 gr. "	0.2220 gr. $\text{P}_2\text{O}_5$ , $\text{Mg}_3$	= 10.47% $\text{P}_2\text{O}_5$
0.8822 gr. "	0.5774 gr. $\text{PtCl}_6\text{K}_3$	= 12.70% $\text{K}_2\text{O}$
1.4517 gr. lost on ignition with	$\text{WO}_3\text{Na}_2$ 0.1349 gr.	= 9.29%

The analyses correspond with the formula

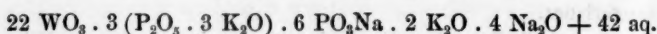


which requires:

		Calc'd.	Found.
22 $\text{WO}_3$	5104	62.36	62.25
6 $\text{P}_2\text{O}_5$	852	10.41	10.47
11 $\text{K}_2\text{O}$	1038	12.68	12.70
7 $\text{Na}_2\text{O}$	434	5.31	5.29
42 $\text{H}_2\text{O}$	756	9.24	9.29
	8184	100.00	

The solution of this salt in chlorhydric acid gives, with magnesia-mixture and ammonia, a precipitate which appears to contain ammonio-magnesian phosphate and magnesian metaphosphate. It is of course possible that a portion of the metaphosphoric acid may have been converted into orthophosphoric acid by the act of solution in chlorhydric acid. I know of no method by which really reliable determinations, either qualitative or quantitative, can be made in compounds of this kind. In the analysis above, the salt was evaporated several times with strong sulphuric acid, and the phosphoric acid then determined with magnesia-mixture. The total quantity of base in the salt

is exactly sufficient to saturate six molecules of orthophosphoric acid, but the salt certainly contains at least a part of the phosphorus as metaphosphoric oxide. We may perhaps assume that the two modifications are equally divided between the bases, and the formula may then be written



The subject of course requires further investigation.

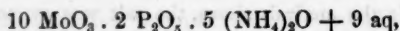
#### MONOMETAPHOSPHO-MOLYBDATES.

The salts belonging to this series appear also to belong to two different classes, which may be simply distinguished as crystalline and gummy salts. Both these classes are readily converted by acids into orthophospho-molybdates. Up to the present time I have made only a preliminary study of these compounds.

10 : 2 : 5 *Ammonic Monometaphospho-molybdate*. — When glacial phosphoric acid is neutralized with ammonia, and the solution is mixed with one of 14 : 6 ammonic molybdate, no precipitate is formed, but on evaporation a thick, nearly colorless gummy mass is formed. On standing for some time, this is almost completely converted into a crystalline mass. This may be drained, redissolved in water, in which it is very soluble, and recrystallized several times from very concentrated solutions. It then presents very beautiful, perfectly colorless, flat tabular crystals. The solution gives at once, with nitric acid, a precipitate of yellow orthophospho-molybdate; with magnesia-mixture and ammonia, a precipitate very different from ammonio-magnesian orthophosphate. Argentic nitrate gives a flocky-crystalline precipitate; baric and thallous nitrates give beautiful white feathery-crystalline salts; mercurous nitrate gives a pale flocky-crystalline precipitate, while cuprous sulphate forms none. Of this salt,

1.4314 gr.	gave 0.3002 gr. $\text{P}_2\text{O}_5$	$\text{Mg}_2 = 13.41\%$	$\text{P}_2\text{O}_5$
0.8385 gr.	" 0.1022 gr. $(\text{NH}_4)_2\text{O}$	$= 12.19\%$	
1.4016 gr.	lost 0.2776 gr.	$= 19.81\%$	

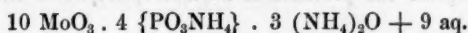
The analyses agree with the formula



which requires:

		Calc'd.		Found.	
10 Mo <sub>2</sub> O <sub>3</sub>	1440	67.10	} 80.33	66.78	} 80.19
2 P <sub>2</sub> O <sub>5</sub>	284	13.23		13.41	
5 (NH <sub>4</sub> ) <sub>2</sub> O	260	12.12		12.19	
9 H <sub>2</sub> O	162	7.55		7.62	
	2146	100.00			

The formula may be more advantageously written



Empirically, this salt has, except as regards water of crystallization, the same formula as the acid 10 : 2 orthophospho-molybdate, which I have already described.

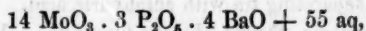
#### HEXAMETAPHOSPHO-MOLYBDATES.

The single salt of this series which I have thus far obtained will serve as an example, and I hope as an incentive to further study.

14 : 3 : 4 *Baric Hexametaphospho-molybdate*. — Sodid hexametaphosphate, obtained by heating the so-called microcosmic salt until a clear colorless glass is obtained, gives a white colorless crystalline salt with baric chloride, which, after washing with cold water, readily dissolves in an excess of a solution of 14 : 6 ammonic molybdate. After a short time the clear filtered solution deposits an abundance of beautiful colorless acicular crystals. This salt cannot be perfectly decomposed by boiling with a solution of mercurous nitrate. Nitric acid dissolves it to a turbid liquid, with formation of a yellow powder. After boiling with the acid, ammonic molybdate gives the characteristic yellow crystalline precipitate, indicating the presence of orthophosphoric acid. Of this salt,

1.0140 gr. lost on ignition with  $\text{WO}_3\text{Na}_2$  0.2463 gr. = 24.31%  
 1.8970 gr. gave 0.4286 gr.  $\text{SO}_4\text{Ba}$  = 14.84% BaO  
 2.0403 gr. “ 0.3454 gr.  $\text{P}_2\text{O}_5\text{Mg}_2$  = 10.83%  $\text{P}_2\text{O}_5$ .

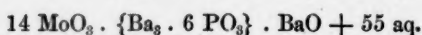
The formula appears to be



which requires :

		Calc'd.	Found.
14 MoO <sub>3</sub>	2016	49.86	50.02
3 P <sub>2</sub> O <sub>5</sub>	426	10.53	10.83
4 BaO	612	15.13	14.84
55 H <sub>2</sub> O	990	24.48	24.31
	4044	100.00	

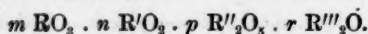
I give this formula with much reserve, and only as probably correct. To express the presence of hexametaphosphoric oxide, it may be written



I shall return to the subject at another time.

#### STANNO-PHOSPHO-TUNGSTATES.

The vanadico-vanadio-tungstates and vanadico-vanadio-molybdates which I have described furnish instances of compounds embraced under the general formulas



I shall show that the compounds belonging to this type are very numerous, and frequently very well defined. For the present, it will be sufficient to cite two new series of hitherto undescribed salts, my object being to direct the attention of other chemists to a new field of investigation, and to point out methods of preparation and of analysis which may facilitate their work.

Stanno-phospho-tungstates are formed when the stanno-chlorides of ammonium or of the alkaline metals are mixed in solution with acid alkaline tungstates. They are colorless crystalline salts, so far as studied. As a representative of this series we may take the ammonium salt.

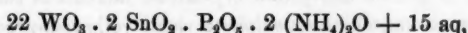
*Analytical Methods.* — In these salts the three higher oxides may be determined together by precipitation with mercurous nitrate and mercuric oxide, but the ignited oxides should be evaporated once or twice with nitric acid to oxidize any reduced tin. Tin may be separated as metal by fusion with potassic cyanide, and phosphoric oxide may be determined after separating tin with sulphydric acid.

*22 : 2 : 1 : 2 Ammonic Stanno-phospho-tungstate.* — When a solution of stanno-chloride of ammonium is poured into a clear cold solution of

24 : 1 sodic phospho-tungstate ( $24 \text{ WO}_3 \cdot \text{P}_2\text{O}_5 \cdot 2 \text{ Na}_2\text{O} + 27 \text{ aq}$ ), a beautiful white crystalline precipitate is formed at once. This is but slightly soluble in boiling water. By long boiling with baric chloride, argentic nitrate, or mercurous nitrate, the salt gives crystalline compounds, which in the cases of the barium and silver salts are colorless; in that of the mercurous salt, yellow. So far as can be determined without quantitative analyses, there appears to be in these cases only a simple double decomposition. For analysis the ammonium salt was thoroughly washed with cold water on the filter-pump, drained, and dried on woollen paper. Of this salt,

1.3577 gr. lost on ignition with $\text{WO}_3\text{Na}_2$	0.0833 gr. =	6.14 %
1.2921 gr. " " without "	0.0812 gr. =	6.29 %
1.6822 gr. gave 0.0646 gr. Sn		= 4.88 % $\text{SnO}_2$
1.1596 gr. " 1.0850 gr. oxides		= 93.57 %
1.1826 gr. " 0.0443 gr. $\text{P}_2\text{O}_5\text{Mg}_2$		= 2.39 %
0.9575 gr. " 0.0182 gr. $(\text{NH}_4)_2\text{O}$		= 1.89 %

The analyses correspond well with the formula



which requires :

22 $\text{WO}_3$	5104	86.21	86.30
2 $\text{SnO}_2$	300	5.06	4.88
$\text{P}_2\text{O}_5$	142	2.39	2.39
2 $(\text{NH}_4)_2\text{O}$	104	1.75	1.89
15 $\text{H}_2\text{O}$	270	4.59	4.24
	<hr/> 5920	<hr/> 100.00	<hr/> 99.70

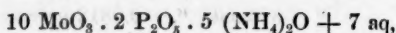
#### STANNO-PHOSPHO-MOLYBDATES.

The salts of this series are formed under precisely the same conditions as the corresponding stanno-phospho-tungstates. It is at least probable that it will be found that the two classes of salts may be formed under other conditions, as, for example, by boiling stannic oxide with phospho-tungstates and phospho-molybdates, or by digesting stanno-tungstates and stanno-molybdates with alkaline phosphates or with phosphoric acid; but I have made no experiments to determine these points.

*Analytical Methods.* — Tin may be determined in these salts by fusion with potassic cyanide, provided that, as in the case of the sepa-

ration of antimony from tungsten and from molybdenum, a sufficient quantity of an alkaline carbonate is added to convert all the higher oxides present into neutral salts. Under these circumstances, no insoluble compound of molybdenum is formed, and the tin separates in bright metallic globules. Phosphoric acid may be determined in these salts after separating the whole of the tin and the greater part of the molybdenum by means of sulphydric acid. Molybdic oxide is estimated most advantageously by difference.

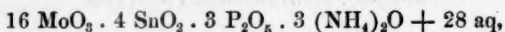
16:4:3:3 *Ammonic Stanno-phospho-molybdate*. — When a solution of stanno-chloride of ammonium,  $\text{SnCl}_6(\text{NH}_4)_2$ , is poured into a hot solution of acid ammonic phospho-molybdate,



a fine bright yellow crystalline precipitate is formed, which quickly settles and leaves a colorless solution. The salt is almost insoluble, even in boiling water, and may perhaps find an application in the separation and quantitative estimation of tin. On boiling with mercurous nitrate it gives a buff-yellow crystalline mercurous salt. Under the same circumstances cupric sulphate yields yellowish-green crystals, and argentic nitrate a very pale yellow, not distinctly crystalline salt. An excess of ammonia readily decomposes the salt with separation of a white gelatinous mass. Of this salt,

0.8648 gr. gave	0.1023 gr. metallic tin	= 15.19 %	$\text{SnO}_2$
2.3780 gr. "	0.3865 gr. $\text{P}_2\text{O}_5$	= 10.40 %	$\text{P}_2\text{O}_5$
1.2021 gr. "	0.2016 gr. "	= 10.73 %	"
1.0130 gr. "	0.3839 gr. $(\text{NH}_4)_2\text{O}$	= 3.79 %	
1.7170 gr. lost on ignition	0.2793 gr.	= 16.27 %	

The analyses give the formula

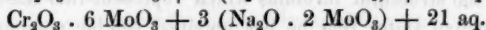
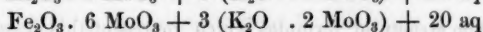


which requires :

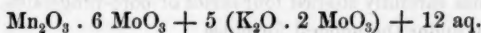
		Calc'd.	Found.
16 $\text{MoO}_3$	2304	57.75	57.97 (diff.)
4 $\text{SnO}_2$	600	15.04	15.19
3 $\text{P}_2\text{O}_5$	426	10.67	10.73 10.40
3 $(\text{NH}_4)_2\text{O}$	156	3.91	3.79
28 $\text{H}_2\text{O}$	504	12.63	12.48
	3990	100.00	

## ALUMINO-MOLYBDATES.

Heinrich Struve,\* in 1854, described a remarkable series of salts, which he regarded simply as double molybdates of the sesquioxides of aluminium, iron, manganese, chromium, and ammonia, potash, or soda. These salts were embraced under two different types, particular aluminic, ferric, and chromic salts, having respectively the formulas



The manganic salt, on the other hand, was represented by



Parmentier † has recently added a new term to this series, the type being



The true character of these compounds could not be understood at the time of their discovery. I find that in solutions of the salts described by Struve, potassium or ammonium may be directly replaced by other metals or by alkaloids, — a fact which was, however, noticed by Struve himself. In addition, — and this is of more importance, — I find that there are series which contain the sesquioxides named with phosphoric and molybdic oxides, so that we have classes of ferro-phospho-molybdates, etc. From my point of view, the compounds in question may be classed under three types, of which the following will serve as representatives: —

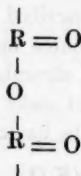
Alumino-dodeka-molybdates,	$\text{Al}_2\text{O}_3 \cdot 12 \text{MoO}_3 \cdot 6 \text{R}_2\text{O}$
Ferrico-dodeka-molybdates,	$\text{Fe}_2\text{O}_3 \cdot 12 \text{MoO}_3 \cdot 6 \text{R}_2\text{O}$
Chromico-dodeka-molybdates,	$\text{Cr}_2\text{O}_3 \cdot 12 \text{MoO}_3 \cdot 6 \text{R}_2\text{O}$
Manganico-hekkaideka-molybdates,	$\text{Mn}_2\text{O}_3 \cdot 16 \text{MoO}_3 \cdot 5 \text{K}_2\text{O} \cdot \text{H}_2\text{O}$ + 11 aq
Alumino-deka-molybdates,	$\text{Al}_2\text{O}_3 \cdot 10 \text{MoO}_3 \cdot 2 \text{R}_2\text{O}$
Ferrico-deka-molybdates,	$\text{Fe}_2\text{O}_3 \cdot 10 \text{MoO}_3 \cdot 2 \text{R}_2\text{O}$
Chromico-deka-molybdates,	$\text{Cr}_2\text{O}_3 \cdot 10 \text{MoO}_3 \cdot 2 \text{R}_2\text{O}.$

All these classes of salts containing oxides corresponding to chlorides of the type  $\text{R}_2\text{Cl}_6$  are very much less stable than compounds containing

\* Petersburg Acad. Bull., xii. 142.

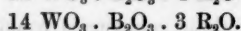
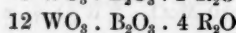
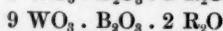
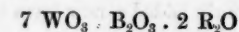
† Comptes Rendus, xcv. 839.

oxides of the types  $R_2O_5$ ,  $RO_2$ , and  $R_2O_3$  (corresponding to chlorides  $RCl_3$ ). We may assume provisionally that the component



enters into the structural formulas which represent this class of compounds. Struve states that he has obtained similar compounds containing tungsten, but these have not been described.

Klein\* has carefully studied four series of boro-tungstates, embraced respectively under the general formulas



Since boron is the lowest term in the third column of the periodic series, aluminum being the next higher, it would seem probable that the oxides which correspond to still higher terms in the same column will form similar compounds. Chromium, manganese, iron, nickel, and cobalt may be regarded as higher harmonics of aluminum, and at least three of these form analogous series. It still remains to study the relations of the oxides of the cerium and yttrium groups to molybdic and tungstic oxides, since these correspond to chlorides of the type  $RCl_3$ , and yet differ in a very marked degree from oxides like  $As_2O_3$ ,  $Sb_2O_3$ , etc. I have made some progress in this investigation and will in another paper give my results in detail.

#### GENERAL CONCLUSIONS.

The formulas and details which I have given in the present installment of my work appear to justify the following general conclusions.

1. Vanadic pentoxide unites with phosphoric or arsenic pentoxides in various proportions to form well-defined complex acids. In some, at least, of these, we seem to have series in which vanadic pentoxide

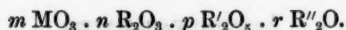
\* Bull. de la Société Chim., [2.] xxxvi. 547, xxxvii. 202.

plays the same part as tungstic or molybdic teroxide, or, in other words, appears to enter the compound as  $V_2O_3 \cdot O_3$ .

2. Compounds of vanadic pentoxide, vanadic dioxide, and phosphoric or arsenic pentoxide, may be formed, possessing properties analogous to those of the compounds of tungstic or molybdic teroxides with pentoxides and dioxides.

3. The series of oxides  $P_2O_3$ ,  $As_2O_3$ ,  $Sb_2O_3$ , unite with tungstic and molybdic oxide to form well-defined series of complex acids. In these the ratio of the number of molecules of the oxides of the types  $R_2O_3$  and  $MO_3$  is much lower than in the cases of the compounds which contain orthophosphoric or ortho-arsenic acids.

4. Compounds exist which contain one oxide of the  $R_2O_3$  (or  $RO_3H_3$ ) and one of the type  $R'_2O_5$  united to tungstic or molybdic oxide, the general formula being



5. Compounds exist which contain acids of the types  $RO_2H_3$  (hypophosphorous acid, for instance) and  $R'_2O_5$  united to tungstic or molybdic oxides, the general formula being



6. Classes of compounds exist which contain oxides of the types  $RO_2$  and  $R'_2O_5$  united to tungstic or molybdic oxides, the general formula being



where, as in the other general formulas, M represents either tungsten or molybdenum.

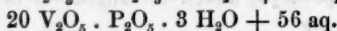
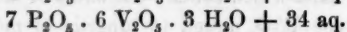
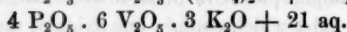
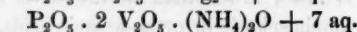
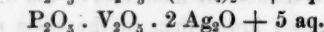
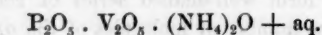
7. Compounds exist which contain pyrophosphoric and metaphosphoric acids in place of orthophosphoric acid. So far as it is possible to judge from the salts analyzed, these contain, or at least may contain, phosphoric and tungstic or molybdic oxides in a lower ratio to each other than in the orthophospho-compounds.

8. Complex acids exist which contain two different modifications of phosphoric acid, as, for instance, metaphosphoric and orthophosphoric acids or oxides.

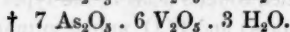
9. The salts described by Struve and by Parmentier establish the existence of a class of complex acids, which contain oxides of the type  $R_2O_3$ , corresponding to chlorides of the type  $R_2Cl_6$ . The true character of these salts is for the first time recognized.

Partly for convenience of reference, and partly to show as distinctly as possible the extent and richness of the field of investigation now opened, I have collected all the formulas of the last and present instalments of my work, prefixing the mark † to those which are in my judgment less certainly established.

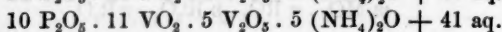
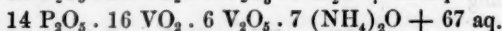
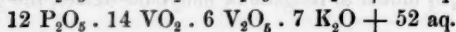
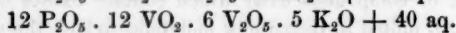
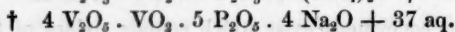
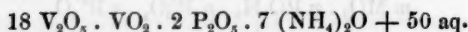
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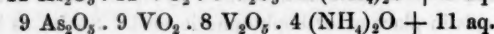
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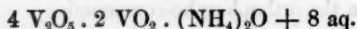
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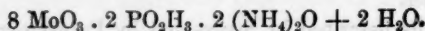
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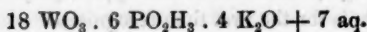
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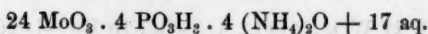
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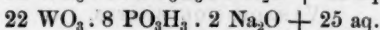
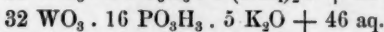
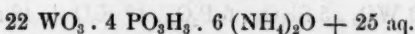
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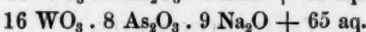
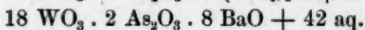
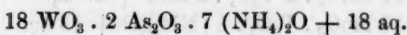
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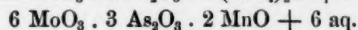
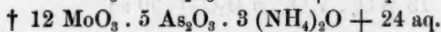
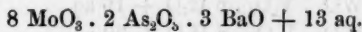
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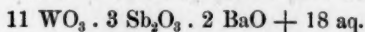
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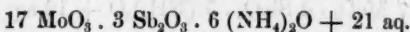
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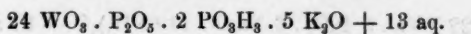
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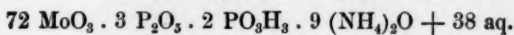
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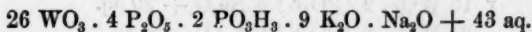
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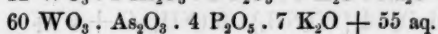
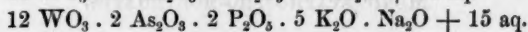
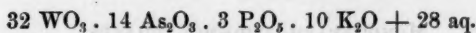
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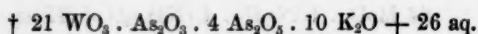
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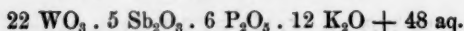
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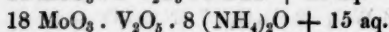
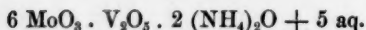
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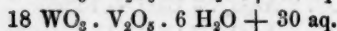
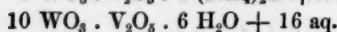
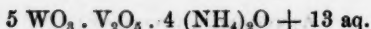
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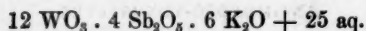
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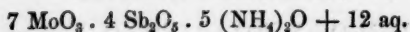
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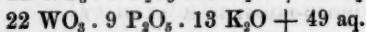
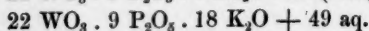
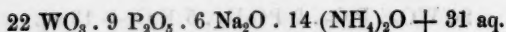
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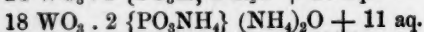
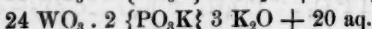
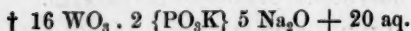
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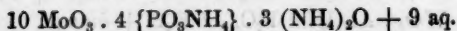
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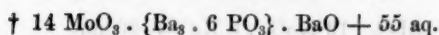
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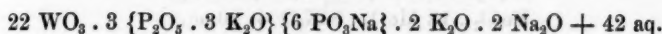
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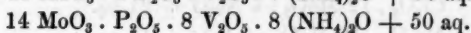
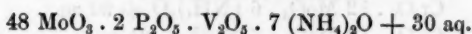
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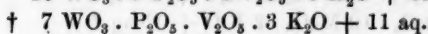
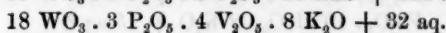
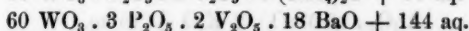
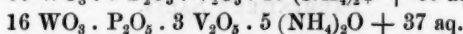
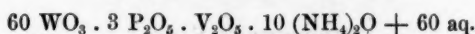
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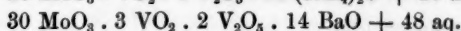
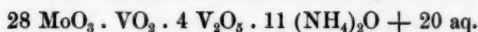
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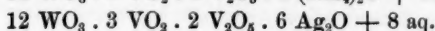
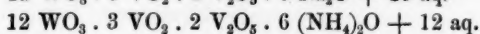
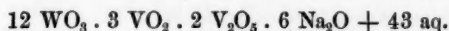
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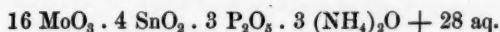
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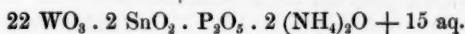
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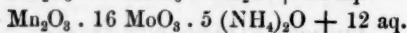
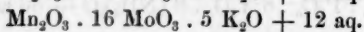
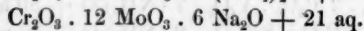
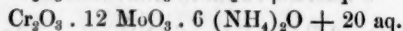
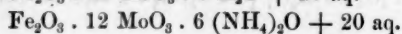
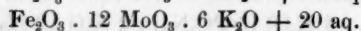
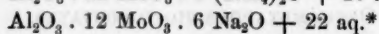
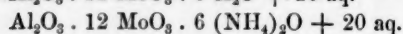
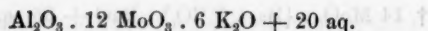


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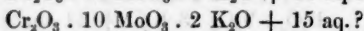
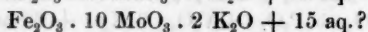


To these I will add the new formulas of the salts described by Struve and Parmentier :—

## STRUVE'S SALTS.



## PARMENTIER'S SALTS.




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\* Gentele, Journal für prakt. Chemie, lxxxi 413.

CAMBRIDGE, July 8, 1885.

(To be continued.)

## IV.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF  
HARVARD COLLEGE.XXV. — ATMOSPHERIC ELECTRICITY AT HIGH  
ALTITUDES.

By ALEXANDER MCADIE, M.A.

Communicated June, 1885.

THE following experiments were made at Blue Hill Observatory during the month of June, 1885. The summit of the Hill has an elevation of 635 feet above sea level, and is therefore the highest point on this section of the Atlantic seaboard. With the exception of the two or three other hills in the range, all the surrounding country is very low and level. The average elevation is below 100 feet. On all sides this low land is well watered, having rivers of fair size and many ponds. For these reasons it was thought profitable to make some observations on the electrical state of the atmosphere, similar in nature to a series made for the United States Signal Service at the Jefferson Physical Laboratory in Cambridge.

The following apparatus was taken to the summit, and employed as hereafter described : —

A Multiple Quadrant Electrometer, designed by Professor Trowbridge, a description of which may be found in the Proceedings of the American Academy, June, 1885.

A portable battery of 100 Beetz cells, set up in series.

A second battery of the same kind, the cells arranged for convenience in sets of ten.

A newly set up Daniell cell.

Two large light kites, silk-covered and tinfoiled on the front face; the longest axes of the kites being over 4 feet.

1,500 feet of strong hemp fish-line, around which in a close spiral was wound No. 22 uncovered copper wire.

50 feet of insulated office wire, and some 10 or 12 feet of rubber tubing, to better insulate the office wire.

One electrometer commutator, and some binding screws.

A condenser, with a capacity of  $\frac{1}{2}$  farad, was also brought up, but when required for use was found to be defective and of no value.

The first observations were made on June 17, at nine A. M.

The first step was to measure the difference between the potential of the air, at a point a few feet out from the observatory walls and about five feet above the ground, and the ground potential. Instead of using the insulated water-dropper devised by Sir William Thomson, I made use of the method employed with success at Cambridge; namely, of dropping water on an insulated metallic plate, and allowing it to fall in drops therefrom. Making the electrometer connections in the way adopted by Thomson and English writers generally, — that is, connecting one set of quadrants with the insulated plate, the other set with the ground, and bringing the needle to a high potential by connecting with the plus pole of a battery of high electromotive force, — the electrometer indicated no appreciable difference between the potential of the air at that point and the potential of the ground. The ground, it may be remarked, was not at the observatory itself, — for the summit is a ledge of solid rock, — but a telephone ground, made of a wire running down the hillside some distance, and connected at different places with metallic plates buried in the earth.

Using the method adopted by Mascart in making the electrometer connections, — that is, connecting one set of quadrants to the plus pole of the 100-cell battery, and the other set of quadrants to the negative pole of the same battery, while the needle is connected with the insulated plate or body whose potential is to be determined, — no appreciable deflection due to the difference between the potentials of the air and ground could be noticed. The insulated plate has to be disconnected, and in its stead the ground substituted in order to ascertain this difference of potential. The electrometer is designed to measure only where differences of potential exist that are of considerable value. The needle of the electrometer carries a fine aluminium pointer, allowing one to read the deflections directly.

In the mean while, the kite having been raised to an elevation of 200 feet, the wired kite-string was now connected with one set of quadrants, and the other set connected with the ground. The needle was connected with the plus pole of the 100-cell Beetz battery, the other pole being grounded. Great care was taken to insulate very thoroughly the kite-string, as with electricity of high tension ordinary methods of insulation are not sufficient. Instantly on making connection, the needle was deflected with a considerable impulse beyond the

limit of the scale (25 scale divisions), and until stopped by the side of the case of the instrument. The deflection indicated a very high positive potential for the air in the vicinity of the kite. To decrease the sensibility of the instrument, the battery charging the needle was reduced from 100 cells to 10 cells, and finally to a single cell. The Beetz battery of 100 cells has a difference of potential between its plus and minus poles of about 100 volts. The needle-pointer being at 0, the plus pole of the battery being connected to one set of quadrants, caused a deflection of 5.5 scale divisions. Connecting the insulated kite-string to the same terminal, the aluminium pointer was deflected with force to the side of the case. The least value of the difference between the kite potential and the ground was about 500 volts. The wind at this time was blowing freshly from the northwest, and the kite was seemingly stationary. Touching the ground wire, for a second, to the kite wire, a small spark about one twentieth of an inch in length was obtained. This, of course, discharged the wire, and the pointer returned to 0, returning, however, almost at once, again to the side of the case. In the hope of getting the deflection within the limits of the scale of the instrument, the quadrants connected with the ground were instead connected with the plus pole of the 100-cell Beetz battery. The deflection under this arrangement would represent the excess value of the air potential over that of the battery terminal. The deflection, however, still remained off the scale, though evidently not very distant. This deflection was maintained all the forenoon. The sky was covered with a low pallium of dark stratus clouds, and the weather was generally muggy and threatening. At three P. M. the kite was sent up as before. The same character of deflection prevailed, and the sparks obtained on connecting the ground with the kite wire were larger and as frequent as in the morning. The shock felt on touching these two wires with the fingers slightly moistened was about the same as one gets from a small-sized Leyden jar. The weather had cleared up, and it was now a clear and pleasant June afternoon. The wind was less steady than in the morning, coming more in puffs. In consequence of this, the kite was less steady, and kept rising and falling. Every time, without exception, when the kite would rise, the needle indicated an increase in the potential; and, on the other hand, as regularly as the kite fell the deflection decreased. When the kite would get apparently within 100 feet of the ground, the deflection would often fall to 8, 10, and sometimes less, of the scale divisions. The movements of the kite were told from watching the movements

of the needle, and about as quickly as they could be seen from without.

On June 18, at 2 h. 30 m., P. M., these experiments were repeated. As before, no difference could be detected between the potential of the air a few feet from the ground, and that of the ground. It is to be remembered, however, that in the present adjustment of the electrometer, a difference equivalent to two volts was the minimum difference that could be detected. With the same instrument, adjusted for greater sensitiveness, employing the same methods, I have found in another locality a difference equivalent to a volt and more between a point in air 10 feet from the ground and the ground itself. The sky had been perfectly cloudless for many hours, and was now without clouds, except one or two very small rounded cumuli in the east. These also in the course of an hour disappeared, and the sky was again cloudless. The height of the kite was determined experimentally, by sending up a carrier on the kite-string, to which was attached thread, with markers at certain distances, made of folded wrapping paper, and of just sufficient weight to keep the thread perpendicular. The distance between the last marker and a level line of sight from the summit was estimated, and added to the known length of thread. My own carrier device having failed, Mr. Willard Gerrish, of the Observatory, suggested a conical-shaped carrier, which answered well. When the kite was about 350 feet high, the needle was deflected off the scale, but did not press against the side of the case of the instrument. When the kite was about 200 feet high, the deflections were in the neighborhood of 10, and variable in character. At this time, then, it was easily possible to notice and record the fluctuations in the value of the potential of the air. At times the needle would start suddenly and swing off the scale; sometimes remaining off, sometimes immediately returning. At other times it would fall to 5, 7, or 8, and either remain at these figures for a while, or vary greatly therefrom.

At 4 h. 30 m., with a cloudless sky, the kite being at a height of 300 feet, the deflection was 23+. The kite was then pulled down until only about half as high as before, and the average deflection was 15+. At 4 h. 50 m., the kite being about 400 feet high, the length of kite-string being about 700 feet, and the distance between the kite and the ground beneath it about 1,000 feet, there being a deep glen between this and the next hill, the deflection was off the scale, and apparently much greater than when at 300 feet. The sparks obtained by presenting the ground-wire to the kite-wire were larger than before,

being about one eighth of an inch in length. The sky was perfectly cloudless at this time. As the kite remained very steady, it was fastened, and allowed to remain up until near eleven o'clock. The deflection of the needle was observed at frequent intervals, and the needle then brought back to the zero by connecting with the ground.

At eight P. M. the kite was more to the northeast than before, but at about the same elevation. The deflections, however, were much less than during the rest of the day, and for the most part within the scale limits. The needle kept constantly moving, but with little of the vigor it had previously shown. The character of the deflections may be illustrated by the following record for a single minute:—

Time. June 19. 1885, P. M.	Deflection.	Character.	Equivalent in Volts to
h. m. s.			
8 4 0	24+	Steady.	Over 500
10	10	Variable.	" 200
20	8	Decreasing steadily.	" 150
30	15	Very variable.	" 300
40	15	{ Variable, increasing } { and decreasing. }	" 300
50	8 to 15	Variable.	" 150
8 5 0	10		" 200

The movements of the kite at this time appeared to be very slight, and one would be apt to suppose too small to account for the great potential changes. But it must be noticed that the movements of the kite, as far as they could be made out, were always in the proper direction to correspond with the character of the potential changes; that is, a rise in the position of the kite was attended with an increasing potential, and a fall attended with a decreasing potential.

At 8 h. 20 m. the deflection was very steady in character, and about 18. The potential indicated by that deflection was not sufficient to give a spark. Fifteen minutes later fair-sized sparks could be obtained at very short intervals. At nine o'clock the same condition prevailed. At ten o'clock the sparks were larger and more frequent. The sky during the whole time was cloudless.

The morning of June 19 was cloudless but hazy, and there was not sufficient wind to fly the kite. In the late afternoon, the wind having freshened from the southwest, the kite was raised to an elevation of about 500 feet above the summit. The kite remaining steady, the deflection was beyond the range of the instrument, and evidently greater than had yet been obtained. Large sparks could be obtained every few seconds by presenting the ground-wire to the kite-wire.

The observatory at Blue Hill is provided with a self-registering anemoscope and a self-registering anemometer. It was originally intended to get a record of the potential variations, and compare it with the records of these two instruments. Unfortunately, both had to be returned to the maker for alterations, because of changes made in the building. It also became apparent that some form of self-recording electrometer was needed. I believe that by means of self-recording instruments the subject of atmospheric electricity can be most advantageously studied. The main purpose in these experiments was to show that it is possible to get some knowledge of the electrical condition of the air at a distance from the ground, with the imperfect means now at our command.

The one point of striking interest in these experiments is the obtaining evidence of this high electrical potential in a sky free from clouds. It will perhaps afford an argument against the necessity of considering condensation in explaining the origin of atmospheric electricity.

It may still be questioned whether these experiments prove that the potential of the air is positive, and increases steadily with increase in elevation. The effects observed may possibly be due to the friction of the air against the tin-foiled kite. My own opinion inclines to the former belief. Questions of this nature, however, can be definitely settled by the results of many and long observations. To accomplish these it is indispensable that a self-recording electrometer be devised, so that the records obtained may be directly comparable with the continuous records of the more prominent meteorological conditions.

I am much indebted to Mr. A. Lawrence Rotch, of the Observatory at Blue Hill, for assistance in carrying on these experiments.

CAMBRIDGE, MASS.

## V.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.

## ON SUBSTITUTED PYROMUCIC ACIDS.

## FIRST PAPER.

BY HENRY B. HILL AND CHARLES R. SANGER.

Communicated November 12, 1884.

## ON BROMPYROMUCIC ACIDS.

ALTHOUGH pyromucic acid has long been known and has been made the subject of many investigations, its behavior toward the halogens has been studied by but few chemists. As early as 1837 Malaguti\* showed that ethyl pyromucate, when treated with dry chlorine, took up four atoms of chlorine forming the ethyl ether of pyromucic tetrachloride. This ether he treated with potassic hydrate, but isolated no product resulting from this decomposition. In 1865 Schmelz and Beilstein† studied the action of aqueous chlorine and bromine upon the acid, and described the resulting four-carbon compounds mucochloric and mucobromic acids. A few years later Limpricht,‡ with several of his pupils, pursued the subject further in the same direction, and isolated, among the products formed by the action of bromine and water upon pyromucic acid, fumaric acid, and its half aldehyde; they made, however, no experiments concerning the action of dry bromine. Toennies,§ working in Baeyer's laboratory, in 1878, prepared the pyromucic tetrabromide by the action of dry bromine upon pyromucic acid, and found that it could be converted into a dibrompyromucic acid melting at 184–186° by the action of alcoholic potash. Toennies did not publish, however, any very extended description of this acid, although he mentions its stability in resisting the action of various oxidizing

\* Ann. Chim. Phys., lxiv. 282; lxx. 371.

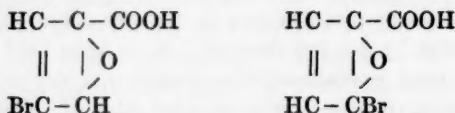
† Ann. Chem. u. Pharm., Suppl., iii. 276.

‡ Ann. Chem. u. Pharm., clxv. 253.

§ Berichte d. deutsch. chem. Gesellsch., xi. 1086; xii. 1203.

agents, and describes a derivative resulting from the action of bromine water, to which he gives the formula  $C_4H_2Br_2O_2$ . By heating the pyromucic tetrabromide he also obtained an acid melting at  $180^\circ$ , to which he assigned no formula, but which from his analyses was evidently a monobromopyromucic acid.

About the time of Toennies's first publication, Schiff and Tassinari\* described two acids which they had obtained by allowing one molecule of bromine to act upon ethyl pyromucate, and decomposing the product thus obtained by alcoholic potash. These acids contained but one atom of bromine, one melted at  $180^\circ$  the other at  $157^\circ$ , and they were named by Schiff and Tassinari the  $\alpha$  and  $\beta$  monobromopyromucic acids. The only statement which they make, beyond a mere description of the physical properties of the two acids, is that one acid may be converted into the other by continued boiling with concentrated hydrochloric acid. This change they consider analogous to the conversion of  $\beta$ -bromocinnamic acid into  $\alpha$ -bromocinnamic acid under similar circumstances, and following this analogy they assign to the two acids the formulæ



In a paper published rather more than a year after the appearance of a preliminary note upon this subject by one of us,† Canzoneri and Oliveri,‡ without in any way alluding to this previous publication, described certain salts of the dibromopyromucic acid of Toennies and of one of the monobromopyromucic acids of Schiff and Tassinari, while they showed that the isomeric acid melting at  $157^\circ$  had no real existence. Our own experiments had already led us to the same conclusion.

Since of the various acids which could be formed by the replacement of the hydrogen atoms of pyromucic acid by halogens at most but three had been prepared, and none of these had been studied in any detail, we undertook the preparation and study of the bromopyromucic acids. In the preparation of pyromucic tetrabromide, which first attracted our attention, we found it impossible to prevent completely the evolution of hydrobromic acid. Since Toennies's analysis of a product

\* Berichte d. deutsch. chem. Gesellsch., xi. 842; Gazzetta Chimica, viii. 297.

† Berichte d. deutsch. chem. Gesellsch., xvi. 1130.

‡ Gazzetta Chimica, xiv. 173.

formed by heating the tetrabromide had shown that a monobromopyromucic acid could thus be formed, we attempted to prepare it by heating the tetrabromide carefully in an oil bath. Although bromine was set free together with hydrobromic acid and monobromopyromucic acid was formed, we did not succeed in making the reaction available for the preparation of this acid on a larger scale. If, on the other hand, the bromine was allowed to act upon the pyromucic acid at the outset at higher temperature, there was little difficulty in securing abundant substitution and excellent product. At first we used glacial acetic acid as a solvent to facilitate the reaction, but we afterwards found that we could easily dispense with it, and that we could at our pleasure replace one or two hydrogen atoms in the pyromucic acid by bromine by varying the conditions of the reaction. The monobromopyromucic acid formed in this way melted at  $183-184^{\circ}$ , and appeared to be identical with that already described by Schiff and Tassinari, as far as could be judged from their meagre description, while the dibromopyromucic acid was new and melted at  $167-168^{\circ}$ .

In studying the action of alkalies upon the pyromucic tetrabromide, we found that the product formed was a mixture of two isomeric dibromopyromucic acids, one of which was identical with that formed by the direct action of bromine upon pyromucic acid, while the second melted at  $190-191^{\circ}$ , and was presumably identical with that which Toennies had prepared in the same way, although he had not obtained it in a state of perfect purity. While we have been wholly unable to verify the assertion of Schiff and Tassinari, that a monobromopyromucic acid exists, whose melting-point is  $157^{\circ}$ , we have found that a new monobromopyromucic acid melting at  $128-129^{\circ}$  can be made by the reduction of either of the two dibromopyromucic acids. We have also found it a matter of no difficulty to prepare tribromopyromucic acid, either by direct substitution from one of the dibromopyromucic acids, or by decomposing with alkalies the monobromopyromucic tetrabromide.

These various substituted pyromucic acids are in many respects more stable than pyromucic acid itself, and we have been able to determine the relative position of the several bromine atoms through a study of their oxidation products.

#### $\delta$ -MONOBROMOPYROMUCIC ACID.

Bromine acts upon pyromucic acid readily at  $100^{\circ}$  and forms a monobromopyromucic acid. To insure a satisfactory yield we have

found it necessary to add the bromine slowly, and to take care that no liquid bromine comes in contact with the pyromucic acid. We have accomplished this very conveniently by hanging inside the flask containing the pyromucic acid a small glass cup, so arranged as to catch the liquid dropping from the reverse cooler and drop-funnel with which the flask is fitted. If the flow of the bromine be carefully regulated and the flask heated in a water bath, the process requires little attention. The reaction, however, is not perfectly smooth. Carbonic dioxide is evolved, and, as more or less bromine is unavoidably lost with the escaping hydrobromic acid, considerably more than one molecule of bromine must be added to insure the best result. For 20 grammes of pyromucic acid we have found it best to use 36 grammes of bromine instead of the 28.57 grammes required by theory. When the reaction is over, the product is dissolved in hot water, filtered, and the voluminous leafy crystals which separate on cooling are purified by recrystallization from hot water. If the bromine has not been added with due care the product may contain more or less dibromopyromucic acid, and is deposited then on cooling the hot aqueous solution in fine granular crystals. The dibromopyromucic acid may, however, readily be removed by precipitating an ammoniacal solution with baric chloride and acidifying the filtered solution with hydrochloric acid. We have not succeeded in obtaining perfectly uniform results in the preparation of the acid, and the yield of pure product has varied between 40 and 60 per cent of the theoretical amount. While we have been unable to prove that isomeric monobromopyromucic acids are formed in the reaction, the properties of the  $\beta$ -monobromopyromucic acid subsequently described are such that a small quantity of it, if formed, might easily escape detection.

The acid crystallized from hot water and dried over sulphuric acid gave on analysis the following results:—

- I. 0.2291 grm. substance gave 0.2629 grm.  $\text{CO}_2$  and 0.0322 grm.  $\text{H}_2\text{O}$ .
- II. 0.2571 grm. substance gave 0.2959 grm.  $\text{CO}_2$  and 0.0400 grm.  $\text{H}_2\text{O}$ .
- III. 0.1944 grm. substance gave 0.1912 grm. AgBr.
- IV. 0.1993 grm. substance gave 0.1957 grm. AgBr.
- V. 0.2085 grm. substance gave 0.2051 grm. AgBr.

	Calculated for $\text{C}_5\text{H}_3\text{BrO}_5$ .	I.	II.	Found. III.	IV.	V.
C	31.42	31.30	31.38			
H	1.57	1.56	1.73			
Br	41.89			41.85	41.78	41.86

The  $\delta$ -monobromopyromucic acid crystallizes from water in irregular leafy plates with pearly lustre which melt at  $183-184^\circ$ . It is readily soluble in alcohol or ether, sparingly soluble in cold chloroform or benzol, more freely soluble on heating. In carbonic disulphide or ligroin it is almost insoluble. In cold water it is sparingly soluble, but dissolves freely on heating. The solubility of the acid in water at ordinary temperatures we determined according to the method of V. Meyer. The acid solution was neutralized with baric carbonate and the barium dissolved precipitated with sulphuric acid.

- I. 37.5965 grm. of a solution saturated at  $16.5^\circ$  gave 0.0500 grm.  $\text{BaSO}_4$ .  
 II. 36.6804 grm. of a solution saturated at  $16.5^\circ$  gave 0.0488 grm.  $\text{BaSO}_4$ .

The aqueous solution of the acid saturated at  $16.5^\circ$  therefore contained the percentages:—

I.	II.
0.22	0.22

*Baric  $\delta$ -Monobromopyromucate*,  $\text{Ba}(\text{C}_5\text{H}_2\text{BrO}_3)_2 \cdot 4\text{H}_2\text{O}$ . — By neutralizing an aqueous solution of the acid with baric carbonate we obtained the barium salt in the form of irregular pearly plates which were readily soluble in hot water, more sparingly in cold. The air-dried salt contained four molecules of water,\* most of which it lost over sulphuric acid.

I. 1.2927 grm. of the salt lost at  $105^\circ$  0.1563 grm.  $\text{H}_2\text{O}$ .

II. 1.3857 grm. of the salt lost at  $105^\circ$  0.1676 grm.  $\text{H}_2\text{O}$ .

	Calculated for $\text{Ba}(\text{C}_5\text{H}_2\text{BrO}_3)_2 \cdot 4\text{H}_2\text{O}$ .	I.	Found. II.
$\text{H}_2\text{O}$	12.23	12.09	12.10

I. 0.3394 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1527 grm.  $\text{BaSO}_4$ .

II. 0.4088 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1848 grm.  $\text{BaSO}_4$ .

	Calculated for $\text{Ba}(\text{C}_5\text{H}_2\text{BrO}_3)_2$ .	I.	Found. II.
Ba	26.50	26.44	26.57

\* Canzoneri and Oliveri assign to this salt the formula  $\text{Ba}(\text{C}_5\text{H}_2\text{BrO}_3)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ . Since their analytical data agree with ours, their incorrect formula is evidently due to an error in calculation.

The solubility of the salt in water at ordinary temperatures we also determined.

- I. 8.1035 grm. of a solution saturated at 18° gave on precipitation with  $\text{H}_2\text{SO}_4$  0.1226 grm.  $\text{BaSO}_4$ .
- II. 7.3943 grm. of a solution saturated at 18° gave on precipitation with  $\text{H}_2\text{SO}_4$  0.1122 grm.  $\text{BaSO}_4$ .

The solution saturated at 18° therefore contained the following percentages of the anhydrous salt:—

	I.	II.
	3.36	3.37

*Calcic δ-Monobrompyromucate*,  $\text{Ca}(\text{C}_5\text{H}_2\text{BrO}_3)_2 \cdot 3 \text{H}_2\text{O}$ . — The calcium salt prepared by neutralizing an aqueous solution with calcic carbonate formed small prisms clustered in globular aggregations which were sparingly soluble in cold water, somewhat more readily in hot.

- I. 1.4814 grm. of the air-dried salt lost at 100° 0.1682 grm.  $\text{H}_2\text{O}$ .
- II. 3.1181 grm. of the air-dried salt lost at 100° 0.3534 grm.  $\text{H}_2\text{O}$ .
- III. 0.2135 grm. of the air-dried salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.0614 grm.  $\text{CaSO}_4$ .

	Calculated for $\text{Ca}(\text{C}_5\text{H}_2\text{BrO}_3)_2 \cdot 3 \text{H}_2\text{O}$ .	I.	Found. II.	III.
$\text{H}_2\text{O}$	11.40	11.35	11.33	
Ca	8.44			8.47

- I. 0.3175 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1032 grm.  $\text{CaSO}_4$ .
- II. 0.3939 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1281 grm.  $\text{CaSO}_4$ .

	Calculated for $\text{Ca}(\text{C}_5\text{H}_2\text{BrO}_3)_2$ .	I.	Found. II.
Ca	9.53	9.56	9.57

The solubility of the calcium salt in water we determined by precipitating with ammoniac oxalate the solution prepared according to the method of V. Meyer, and converting the calcic oxalate thus obtained into sulphate by ignition with sulphuric acid.

- I. 17.9259 grm. of a solution saturated at 20° gave 0.0620 grm.  $\text{CaSO}_4$ .
- II. 15.5795 grm. of a solution saturated at 20° gave 0.0528 grm.  $\text{CaSO}_4$ .

The solution saturated at 20° therefore contained the following percentages of the anhydrous salt:—

I.	II.
1.07	1.05

*Argentie δ-Monobrompyromucate*,  $\text{AgC}_5\text{H}_2\text{BrO}_3$ .—The silver salt falls as a crystalline precipitate on the addition of argentic nitrate to an aqueous solution of the free acid. We prepared it, however, by precipitating a solution of the potassium salt with argentic nitrate, and recrystallized the product from boiling water. It formed small clustered plates sparingly soluble even in boiling water, which could be recrystallized without decomposition from hot water.

0.2321 grm. of the salt dried over sulphuric acid gave on precipitation with HBr 0.1465 grm. AgBr.

	Calculated for $\text{AgC}_5\text{H}_2\text{BrO}_3$ .	Found.
Ag	36.24	36.25

*Sodic δ-Monobrompyromucate*,  $\text{NaC}_5\text{H}_2\text{BrO}_3$ .—On neutralizing the acid with sodic carbonate we obtained the sodium salt in the form of small radiated needles which proved to be anhydrous.

- I. 0.4172 grm. of the salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1388 grm.  $\text{Na}_2\text{SO}_4$ .  
 II. 0.6014 grm. of the salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1993 grm.  $\text{Na}_2\text{SO}_4$ .

	Calculated for $\text{NaC}_5\text{H}_2\text{BrO}_3$ .	I.	Found.	II.
Na	10.80	10.78		10.74

*Potassic δ-Monobrompyromucate*,  $\text{KC}_5\text{H}_2\text{BrO}_3$ .—The potassium salt crystallized in irregular flattened prisms which were very soluble in water, and contained no water of crystallization.

- I. 0.3118 grm. of the salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1191 grm.  $\text{K}_2\text{SO}_4$ .  
 II. 0.3384 grm. of the salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1285 grm.  $\text{K}_2\text{SO}_4$ .

	Calculated for $\text{KC}_5\text{H}_2\text{BrO}_3$ .	I.	Found.	II.
K	17.07	17.15		17.05

*Ethyl 8-Monobrompyromucate*,  $(C_2H_5)_3C_3H_2BrO_3$ .—The ethyl ether of the acid can readily be made by heating the acid with absolute alcohol and concentrated sulphuric acid, or by the action of ethyl iodide upon the silver salt\*. It may conveniently be prepared by warming for several hours on the water bath a mixture of four parts of absolute alcohol and three parts of concentrated sulphuric acid with four parts of the acid. A portion of the ether separates while the mixture is still hot, and on cooling and precipitating with water the quantity of ether obtained is nearly equal to that of the acid taken. The ether, washed with a dilute solution of sodic carbonate, and dried with calcic chloride, had a fragrant odor resembling ethyl pyromucate, and boiled between  $234.5^\circ$  and  $236.5^\circ$ , the greater portion showing a constant boiling-point of  $235^\circ$ † (mercury column completely in vapor) under a pressure of 767 mm. Since it retained a slight

\* We attempted at first to prepare this ether by saturating the alcoholic solution of the acid with hydrochloric acid gas. The product which we thus obtained boiled at  $132^\circ$  under a pressure of 20 mm., and showed no signs of crystallization when strongly cooled. An analysis showed that this product contained much too high a percentage of halogen, and the results agreed quite closely with those required by the formula  $(C_2H_5)_3C_3H_4BrCl_2O_3$ .

	Calculated for $(C_2H_5)_3C_3H_4BrCl_2O_3$ .	Found.	
BrCl <sub>2</sub>	51.71	51.84	52.28

This behavior of the acid requires further investigation.

† The thermometer used was a "Zincke" thermometer made by Geissler. It gave the boiling-point of pure naphthaline under a pressure of 769 mm. with the mercury column completely in vapor as  $217.6^\circ$ . According to Crafts (Am. Journal Chemistry, v. 324) this boiling-point is about one degree too low, although it agrees exactly with that taken by Geissler in the graduation of his thermometers. Several years ago I gave the boiling-point of a specimen of ethyl pyromucate prepared by Mr. J. J. Thomsen as  $195^\circ$  under a pressure of 766 mm. (these Proceedings, vol. xvi. (n. s. viii.) p. 160), this boiling-point being materially lower than that given by Malaguti (Ann. Chim. Phys., [2,] lxiv. 279),  $208-210^\circ$ , under a pressure of 756 mm. Since Canzoneri and Oliveri have recently given the boiling-point of the ether as  $205-208^\circ$ , I have thought it worth while to repeat the determination. The thermometer I had previously used was made by Geissler, but I had neglected to determine its correctness above  $200^\circ$  by means of the boiling-point of naphthaline. An entirely different preparation of the ether, which melted at  $34-35^\circ$  (somewhat higher than the old preparation), showed with the above "Zincke" thermometer the constant boiling-point  $195^\circ$  under a pressure of 769 mm., the mercury column being completely in the vapor. The ether was then allowed to stand for eighteen hours with fused calcic chloride, the temperature being for a great part of the time just above the melting-point of the ether. The boiling-point was still found to be constant at  $195^\circ$  under a pressure of 768 mm.

H. B. H.

yellowish tinge after several distillations, we distilled it for analysis under diminished pressure, and found it to boil at 133–134° under a pressure of 31 mm. On cooling, the ether crystallized in clear prisms with bevelled ends. The melting-point of the solidified ether was found to be 17°, and when the liquid ether was cooled to 13°, and a crystal of the solid ether introduced, the thermometer rose to 17°. The specific gravity of the ether at 20° referred to water at the same temperature we found to be 1.528.

Analyses I. and II. were made with substance prepared from the silver salt; III. and IV. from substance made with sulphuric acid.

- I. 0.2171 grm. substance gave 0.1875 grm. AgBr.
- II. 0.1616 grm. substance gave 0.1380 grm. AgBr.
- III. 0.3571 grm. substance gave 0.3042 grm. AgBr.
- IV. 0.3080 grm. substance gave 0.2623 grm. AgBr.

	Calculated for (C <sub>5</sub> H <sub>5</sub> )C <sub>5</sub> H <sub>2</sub> BrO <sub>2</sub>	I.	II.	Found. III.	IV.
Br	36.52	36.76	36.35	36.25	36.23

*δ*-Monobrompyromucamide, C<sub>5</sub>H<sub>2</sub>BrO<sub>2</sub>NH<sub>2</sub>. — Concentrated aqueous ammonia acts but slowly upon the ether in the cold, and several days are necessary to complete the reaction. At 100° in a sealed tube the decomposition is perfect in a few hours, but the yield of the amide is apparently not so satisfactory. The product of the reaction when recrystallized from boiling water forms long shining needles which melt at 144–145°. They are sparingly soluble in cold water, readily in hot, readily soluble in alcohol, ether, chloroform, or in hot benzol, sparingly soluble in cold benzol or carbonic disulphide. For analysis the substance was recrystallized from boiling water and dried over sulphuric acid.

0.7761 grm. substance gave 50.6 c.c. of moist nitrogen at 20°, and under a pressure of 747 mm.

	Calculated for C <sub>5</sub> H <sub>2</sub> BrO <sub>2</sub> NH <sub>2</sub>	Found.
N	7.37	7.46

*δ*-Monobrompyromucic tetrabromide. — When exposed to an atmosphere of bromine, the *δ*-monobrompyromucic acid takes up four atoms of bromine. The addition product is readily soluble in alcohol or ether, is decomposed by water, but may be recrystallized from glacial acetic acid. It forms fine needles which decompose without melting at 173°.

0.1948 grm. substance gave 0.3594 grm. AgBr.

	Calculated for C <sub>5</sub> H <sub>3</sub> Br <sub>5</sub> O <sub>2</sub>	Found.
Br	78.29	78.52

*Action of Bromine and Water.*

Since pyromucic acid itself is readily attacked by aqueous bromine, and converted, according to the conditions of the reaction, into fumaric aldehyd or mucobromic acid, it seemed to us of interest to study the behavior of the  $\delta$ -monobrompyromucic acid under similar conditions. We have found that the products formed vary greatly according to the conditions chosen, but in every case they prove to contain but four carbon atoms.

The acid was suspended in about thirty times its weight of cold water, and the vapor of bromine slowly led in by means of a current of air. Two molecules of bromine were found necessary to complete the reaction. The strongly acid solution, when extracted repeatedly with ether, gave an acid sparingly soluble in cold water, more readily in hot, which, when recrystallized from hot water, proved to be free from bromine. The behavior of this acid on heating showed it to be fumaric acid. Its identity was further established by an analysis of the silver salt.

0.5462 grm. of the salt gave 0.6194 grm. AgBr.

	Calculated for $\text{Ag}_2\text{C}_4\text{H}_2\text{O}_4$	Found.
Ag	65.46	65.13

Beside the fumaric acid could be isolated minute quantities of two acids which contained bromine, and which from their physical properties appeared to be dibromsuccinic and isodibromsuccinic acids. These acids were formed in much larger quantity when the bromine was rapidly added; considerably more than two molecules of bromine were required to complete the reaction, and at the same time a crystalline substance insoluble in water was then formed. The aqueous solution was filtered from this insoluble substance and extracted with ether. The ethereal extract upon evaporation left a white crystalline residue which contained but little fumaric acid, and proved to consist mainly of about equal quantities of two acids, which could be separated by repeated recrystallization from water. The more soluble acid could be obtained by slow evaporation in well-formed rhombic plates which melted at  $165^\circ$ , and which on analysis proved to contain the percentage of bromine required by isodibromsuccinic acid.

I. 0.2434 grm. of substance gave 0.3344 grm. AgBr.

II. 0.2427 grm. of substance gave 0.3305 grm. AgBr.

	Calculated for $\text{C}_4\text{H}_4\text{Br}_2\text{O}_4$	Found.	
		I.	II.
Br	57.97	58.44	57.94

The less soluble acid crystallized from hot water in well-defined prisms, which remained unchanged when heated to  $200^{\circ}$ . An analysis showed this acid to be ordinary dibromsuccinic acid.

0.2468 grm. substance gave 0.3363 grm. AgBr.

	Calculated for $C_4H_4Br_2O_4$ .	Found.
Br	57.97	57.98

The aqueous solution from which the two dibromsuccinic acids had been extracted with ether still contained a certain amount of fumaric acid, which was obtained by evaporation and identified by qualitative tests.

The substance insoluble in water which had been formed by the action of bromine was recrystallized, first from alcohol, then from ligroin, and crystallized in colorless prisms which melted at  $110-111^{\circ}$ . Analysis showed the substance to be dibromfurfurantetrabromide.

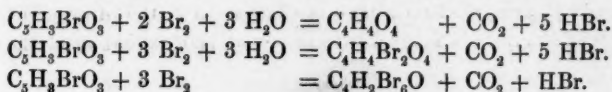
I. 0.7407 grm. substance gave 0.2380 grm.  $CO_2$  and 0.0284 grm.  $H_2O$ .

II. 0.2054 grm. substance gave 0.4259 grm. AgBr.

III. 0.1680 grm. substance gave 0.3476 grm. AgBr.

	Calculated for $C_4H_2Br_6O_4$ .	I.	Found. II.	III.
C	8.79	8.76		
H	0.37	0.43		
Br	87.90		88.22	88.04

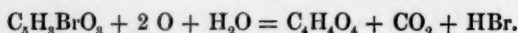
This substance will be more fully studied and the results presented to the Academy at a future time. The action of bromine upon the  $\delta$ -monobrompyromucic acid under the conditions we have chosen may therefore be expressed by the following equations:—



#### *Action of Nitric Acid.*

On warming  $\delta$ -monobrompyromucic acid with dilute nitric acid it is readily oxidized, carbonic dioxide is given off in abundance, and a small quantity of a yellowish oil distils over, which has not yet been further examined. For the complete oxidation of the acid we have found it best to take an equal weight of nitric acid (sp. gr. 1.42), diluted with four times its weight of water. The solution on cooling deposits crys-

tals of fumaric acid, and still more may be obtained by evaporation. The weight of fumaric acid thus obtained amounted to a little more than sixty per cent of that calculated from the equation,



The acid recrystallized from water and dried at  $100^\circ$  gave on analysis the following results:—

0.1728 grm. substance gave 0.2613 grm.  $\text{CO}_2$  and 0.0575 grm.  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_4\text{H}_4\text{O}_4$ .	Found.
C	41.37	41.24
H	3.45	3.70

Beside the fumaric acid could be isolated a small quantity of an acid readily soluble in cold water, whose melting-point suggested the possibility of its being maleic acid. Since at the high temperature which we had employed in oxidation it was to be expected that the maleic acid formed would be almost entirely converted into fumaric acid, we repeated the oxidation with stronger nitric acid (sp. gr. 1.42) and kept the temperature carefully between  $30^\circ$  and  $35^\circ$ . At this temperature the oxidation went on vigorously, and constant cooling was necessary. For complete oxidation three parts of strong nitric acid were found to be advantageous. After the oxidation was complete, the gaseous products of the reaction were removed by a current of air, the solution was then diluted, filtered from a slight flocculent precipitate thus formed, and neutralized with baric hydrate. In this way was precipitated a sparingly soluble crystalline barium salt, which, when recrystallized from hot water and dried by exposure to the air, proved to have the percentage composition of baric maleate.

- I. 1.0940 grm. of the air-dried salt lost at  $158^\circ$  0.0794 grm.  $\text{H}_2\text{O}$ .  
 II. 0.7644 grm. of the air-dried salt lost at  $160^\circ$  0.0551 grm.  $\text{H}_2\text{O}$ .

	Calculated for $\text{BaC}_4\text{H}_2\text{O}_4 \cdot \text{H}_2\text{O}$ .	Found.	
		I.	II.
$\text{H}_2\text{O}$	6.69	7.26	7.21

- I. 0.5036 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.4675 grm.  $\text{BaSO}_4$ .  
 II. 0.2776 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.2579 grm.  $\text{BaSO}_4$ .

	Calculated for $\text{BaC}_4\text{H}_2\text{O}_4$ .	Found.	
		I.	II.
Ba	54.58	54.58	54.62

From the barium salt we made the acid by exact precipitation with sulphuric acid, and recrystallized it first from ether and afterwards from water. The acid thus prepared melted at  $131-132^{\circ}$ ,\* was very soluble in cold water, and by heating with hydrochloric acid in aqueous solution was converted into an acid having all the physical properties of fumaric acid. By the method just described we obtained about fifty per cent of the weight of baric maleate theoretically required; and since the method of separation was necessarily imperfect, we have not hesitated to assume that in the oxidation of  $\delta$ -monobrompyromucic acid with nitric acid maleic acid is the product first formed, and that the fumaric acid obtained in the oxidation at higher temperature results only from the further alteration of this. While we have been unable to prove as yet the formation of maleic acid in the oxidation with bromine, even under the most favorable conditions, it seems to us that there can be little doubt that the reaction in this case is also essentially the same. The occurrence of isodibromsuccinic acid among the products of the action of bromine, while it does not prove this view to be correct, certainly is in its favor.

#### $\beta$ -MONOBROMPYROMUCIC ACID.

From either of the dibrompyromucic acids subsequently described may be obtained by careful reduction a new monobrompyromucic acid isomeric with that already described. Since the dibrompyromucic acid melting at  $167-168^{\circ}$  is more conveniently prepared in large quantity, we have used this in order to obtain material for investigation. We have obtained the best results by dissolving two parts of the acid in four parts of concentrated ammoniac hydrate diluted with fourteen parts of water, and adding one part of zinc dust. The reduction begins at once, the solution becomes hot, and in a few minutes the reaction is completed. When the ammoniacal solution no longer gives with calcic chloride an immediate precipitate of the sparingly soluble calcium salt of the dibrompyromucic acid, it is filtered and acidified with hydrochloric acid. If the reduction has not been carried too far, the solution soon solidifies with fine felted needles of the  $\beta$ -monobrompyromucic acid. For the purification of the acid we have found it best to convert it into the calcium salt, and to reject that portion of the

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\* The melting-point of maleic acid is usually given as  $130^{\circ}$ , but Kékulé has recently given the higher melting-point  $132^{\circ}$ .—Ann. Chem. u. Pharm., cxxiii. 186.

salt which first separates from a dilute solution. The acid obtained by acidifying the concentrated solution we have then recrystallized from hot water. The acid dried over sulphuric acid gave on analysis the following results. The material used in Analysis IV. was made from the dibromopyromucic acid melting at 191–192°.

- I. 0.5336 grm. substance gave 0.6117 grm.  $\text{CO}_2$  and 0.0828 grm.  $\text{H}_2\text{O}$ .  
 II. 0.1996 grm. substance gave 0.1967 grm.  $\text{AgBr}$ .  
 III. 0.2064 grm. substance gave 0.2031 grm.  $\text{AgBr}$ .  
 IV. 0.2115 grm. substance gave 0.2089 grm.  $\text{AgBr}$ .

	Calculated for $\text{C}_6\text{H}_5\text{BrO}_3$	I.	II.	Found. III.	IV.
C	31.42	31.26			
H	1.57	1.72			
Br	41.89		41.97	41.88	42.05

$\beta$ -Monobromopyromucic acid is readily soluble in alcohol or ether, quite soluble in chloroform or benzol, more sparingly soluble in ligroin or carbonic disulphide. It is very readily soluble in hot water, and as the solution cools it separates at high temperatures as an oil; at lower temperatures, in fine silky needles, which melt at 128–129°. On heating, it sublimes readily without decomposition. The solubility of the acid in water at ordinary temperatures we determined by neutralizing the solution with baric carbonate and precipitating with sulphuric acid the barium dissolved.

- I. 21.1125 grm. of a solution saturated at 20° gave 0.1598 grm.  $\text{BaSO}_4$ .  
 II. 15.7586 grm. of a solution saturated at 20° gave 0.1198 grm.  $\text{BaSO}_4$ .

The aqueous solution saturated at 20° therefore contained the following percentages of the acid:—

I.	II.
1.24	1.25

*Baric  $\beta$ -Monobromopyromucate*,  $\text{Ba}(\text{C}_6\text{H}_4\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ .—By neutralizing an aqueous solution of the acid with baric carbonate, and concentrating the solution on the water bath, we obtained the barium salt in the form of irregular leafy scales, which were sparingly soluble in cold water, readily in hot. The air-dried salt lost nothing over sulphuric acid, and proved to contain one molecule of water.

- I. 0.9389 grm. of air-dried salt lost at 120° 0.0334 grm.  $\text{H}_2\text{O}$ .  
 II. 1.9210 grm. air-dried salt lost at 130° 0.0676 grm.  $\text{H}_2\text{O}$ .

	Calculated for $\text{Ba}(\text{C}_5\text{H}_7\text{BrO}_3)_2\text{H}_2\text{O}$ .	Found.	
		I.	II.
$\text{H}_2\text{O}$	3.36	3.56	3.52

- I. 0.8920 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$   
0.4005 grm.  $\text{BaSO}_4$ .
- II. 0.6245 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$   
0.2816 grm.  $\text{BaSO}_4$ .

	Calculated for $\text{Ba}(\text{C}_5\text{H}_7\text{BrO}_3)_2$ .	Found.	
		I.	II.
Ba	26.50	26.39	26.51

The solubility of the salt in cold water we determined according to the method of V. Meyer.

- I. 6.1243 grm. of a solution saturated at  $20^\circ$  gave on precipitation with  $\text{H}_2\text{SO}_4$  0.0581 grm.  $\text{BaSO}_4$ .
- II. 3.3922 grm. of a solution saturated at  $20^\circ$  gave on precipitation with  $\text{H}_2\text{SO}_4$  0.0317 grm.  $\text{BaSO}_4$ .

The aqueous solution saturated at  $20^\circ$  therefore contained the following percentages of the anhydrous salt:—

I.	II.
2.11	2.07

*Calcic  $\beta$ -Monobrompyromucate*,  $\text{Ca}(\text{C}_5\text{H}_7\text{BrO}_3)_2 \cdot 3 \text{H}_2\text{O}$ .—The calcium salt we prepared by neutralizing an aqueous solution of the acid with calcic carbonate. It crystallizes in small clustered branching needles, which are sparingly soluble in cold water, more readily in hot. The salt is permanent in the air, but effloresces over sulphuric acid.

- I. 1.1627 grm. of the air-dried salt lost at  $120^\circ$  0.1314 grm.  $\text{H}_2\text{O}$ .
- II. 1.8043 grm. of the air-dried salt lost at  $120^\circ$  0.2047 grm.  $\text{H}_2\text{O}$ .

	Calculated for $\text{Ca}(\text{C}_5\text{H}_7\text{BrO}_3)_2 \cdot 3 \text{H}_2\text{O}$ .	Found.	
		I.	II.
$\text{H}_2\text{O}$	11.40	11.30	11.34

- I. 0.4784 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$   
0.1534 grm.  $\text{CaSO}_4$ .
- II. 0.5696 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$   
0.1838 grm.  $\text{CaSO}_4$ .

	Calculated for $\text{Ca}(\text{C}_5\text{H}_7\text{BrO}_3)_2$ .	Found.	
		I.	II.
Ca	9.53	9.43	9.49

The solubility of the salt in cold water we determined by precipitating the saturated solution with ammoniac oxalate, and converting the calcic oxalate thus obtained into calcic sulphate by ignition with sulphuric acid.

- I. 11.3923 grm. of a solution saturated at 20° gave 0.0642 grm.  $\text{CaSO}_4$ .  
 II. 11.2016 grm. of a solution saturated at 20° gave 0.0625 grm.  $\text{CaSO}_4$ .

The aqueous solution saturated at 20° therefore contained the following percentages of the anhydrous salt:—

I.	II.
1.74	1.72

*Argentio β-Monobrompyromucate*,  $\text{AgC}_5\text{H}_2\text{BrO}_3$ .—The silver salt is precipitated by the addition of argentic nitrate to an aqueous solution of the acid. For analysis, we prepared it from the sodium salt by precipitation, and purified it by recrystallization from hot water.

0.2503 grm. of the salt gave on precipitation with  $\text{HBr}$  0.1586 grm.  $\text{AgBr}$ .

	Calculated for $\text{AgC}_5\text{H}_2\text{BrO}_3$ .	Found.
Ag	36.24	36.41

*Sodio β-Monobrompyromucate*,  $\text{NaC}_5\text{H}_2\text{BrO}_3$ .—The sodium salt prepared by neutralizing an aqueous solution of the acid with sodic carbonate crystallized in globular masses and proved to be anhydrous.

- I. 0.4338 grm. of the salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1470 grm.  $\text{Na}_2\text{SO}_4$ .  
 II. 0.5577 grm. of the salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1849 grm.  $\text{Na}_2\text{SO}_4$ .

	Calculated for $\text{NaC}_5\text{H}_2\text{BrO}_3$ .	Found.	
		I.	II.
Na	10.80	10.98	10.74

*Potassic β-Monobrompyromucate*,  $\text{KC}_5\text{H}_2\text{BrO}_3$ .—On neutralizing the acid in aqueous solution with potassic carbonate we obtained the potassium salt in the form of flat rectangular plates which proved to be anhydrous.

- I. 0.3443 grm. of the salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1293 grm.  $\text{K}_2\text{SO}_4$ .

II. 0.4727 grm. of the salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1775 grm.  $\text{K}_2\text{SO}_4$ .

	Calculated for $\text{KC}_5\text{H}_7\text{BrO}_3$ .	Found.	
		I.	II.
K	17.07	16.86	16.86

*Ethyl  $\beta$ -Monobrompyromucate*,  $(\text{C}_2\text{H}_5)_2\text{C}_5\text{H}_7\text{BrO}_3$ . — The ethyl ether we have made by the action of ethyl iodide upon the silver salt, and also by heating a solution of the acid in absolute alcohol with concentrated sulphuric acid. It may conveniently be prepared by warming for several hours five parts of the acid with a mixture of five parts of absolute alcohol and three parts of concentrated sulphuric acid. A portion of the ether separates while the mixture is still hot, the rest may be precipitated after cooling by the addition of water. The product, well washed with water and a dilute solution of sodic carbonate, solidifies at low temperatures, and may be purified by repeated melting and pressing with filter-paper the crystals obtained by cooling. The ether crystallizes in transparent clustered prisms, and has a fragrant odor not unlike that of ethyl pyromucate. We found that it distilled without decomposition at  $235\text{--}236^\circ$  (mercury column completely in vapor) under a pressure of 768 mm., and that the greater portion boiled steadily at  $235^\circ$ . The thermometer in the solidifying distillate stood at  $28^\circ$ , while the melting-point, determined in the ordinary way in a capillary tube, we found to be  $28\text{--}29^\circ$ . The ether prepared from the silver salt by the action of ethyl iodide had the same melting-point, and was used in Analysis II.

I. 0.2194 grm. substance gave 0.1888 grm. AgBr.

II. 0.2120 grm. substance gave 0.1820 grm. AgBr.

	Calculated for $(\text{C}_2\text{H}_5)_2\text{C}_5\text{H}_7\text{BrO}_3$ .	Found.	
		I.	II.
Br	36.52	36.64	36.55

*$\beta$ -Monobrompyromucamide*,  $\text{C}_5\text{H}_7\text{BrO}_2\text{NH}_2$ . — From the ethyl ether of  $\beta$ -monobrompyromucic acid can readily be made the corresponding amide by the action of concentrated aqueous ammonia, since the reaction progresses quite rapidly even at ordinary temperatures. The resulting product, when repeatedly crystallized from boiling water, formed fine silky needles which melted at  $155\text{--}156^\circ$ . It was readily soluble in alcohol, quite readily soluble in ether or boiling chloroform, more sparingly soluble in benzol, and almost insoluble in carbonic

disulphide or ligroin. It was readily soluble in hot water, but sparingly soluble in cold water.

0.6771 grm. substance gave 46.5 c.c. of moist nitrogen at 22.5° and under a pressure of 741 mm.

	Calculated for $C_6H_5BrO_2NH_2$ .	Found.
N	7.37	7.74

$\beta$ -monobromopyromucic acid appears to form no stable addition product with bromine. When exposed to the vapors of bromine for two days, we found that it had gained but 30 per cent of its weight, while a gain of 168 per cent was required for the formation of a tetrabromide. This slight gain in weight and the abundant evolution of hydrobromic acid pointed to the formation of a dibromopyromucic acid, for which a gain of 41 per cent was required. The product gave little evidence of decomposition when boiled with water, and was almost wholly soluble in a dilute solution of sodic carbonate. When recrystallized once from glacial acetic acid it melted at 165–166°, and possessed the characteristic properties of  $\beta\delta$ -dibromopyromucic acid. Bromine at ordinary temperatures had therefore replaced one atom of hydrogen by bromine.

#### *Action of Bromine and Water.*

When  $\beta$ -monobromopyromucic acid is treated with bromine in aqueous solution it is rapidly oxidized, and products are formed which are apparently analogous to those formed from pyromucic acid under similar conditions. One or two molecules of bromine were readily taken up in the cold. In either case, the clear aqueous solution, when extracted with ether, yielded viscous oily products which showed no signs of crystallization after standing for days in vacuo over sulphuric acid. The extremely uninviting character of these substances made us unwilling to spend more time upon them at present, more especially since we found that mucobromic acid was formed when three molecules of bromine were employed. The reaction in this case required heat for its completion, and from the concentrated solution mucobromic acid (melting-point 120–121°) crystallized on cooling. Since it is probable that the aldehyde acid with one bromine atom corresponding to mucobromic acid is formed by the action of two molecules of bromine, we hope in the future to study the reaction further.

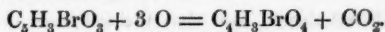
*Action of Nitric Acid.*

$\beta$ -monobrompyromucic acid is readily oxidized by dilute nitric acid. In order to determine the product formed, we heated the acid with twice its weight of concentrated nitric acid (sp. gr. 1.42) diluted with five times its weight of water. After the oxidation was complete, we extracted the solution thoroughly with ether, and obtained, on evaporating the ether, a white crystalline acid which was readily soluble in water. After recrystallization from water it melted at 176–177°, and gave a percentage of bromine, which showed it to be monobromfumaric acid (isobrommaleic acid).

0.2300 grm. substance gave 0.2218 grm. AgBr.

	Calculated for $C_4H_3BrO_4$	Found.
Br	41.03	41.04

By oxidation with nitric acid monobromfumaric acid had therefore been formed according to the equation,

**ETHYL PYROMUCATE WITH ONE MOLECULE OF BROMINE.**

We have made six fruitless attempts to prepare a monobrompyromucic acid melting at 156–157°, according to the method described by Schiff and Tassinari,\* by the addition of one molecule of bromine to ethyl pyromucate, and the decomposition of the product thus obtained by an alcoholic solution of potassic hydrate. Aside from the  $\delta$ -monobrompyromucic acid, which could readily be isolated, we have been able to find only the two isomeric dibrompyromucic acids hereafter described which result from the decomposition of the tetrabromide of the ethyl ether. In separating these two acids we followed the method which we had already found most efficacious, namely, the fractional crystallization of the calcium salts, but in other respects we adhered strictly to the directions given by Schiff and Tassinari. The acid obtained from the less soluble calcium salt melted at 166–167°, and crystallized from water in the twinned forms characteristic of the  $\beta\delta$ -dibrompyromucic acid.

0.1444 grm. substance gave 0.2020 grm. AgBr.

	Calculated for $C_6H_2Br_2O_8$	Found.
Br	59.26	59.53

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\* Gazzetta Chimica, viii. 298.

From the more soluble calcium salt we obtained the  $\beta\gamma$ -dibromopyromucic acid melting at 190–192°, which gave on analysis the proper percentage of bromine.

0.1955 grm. substance gave 0.2723 grm. AgBr.

	Calculated for $C_8H_2Br_2O_8$ .	Found.
Br	59.26	59.29

Furthermore, it was not difficult to isolate in considerable quantity an acid containing but a trace of bromine, which melted at 129–130°, and which possessed in other respects the character of pyromucic acid. Our observations agree closely with those described by Canzoneri and Oliveri in the paper already mentioned,\* with the single exception that they appear to have overlooked entirely the formation of the second dibromopyromucic acid melting at 167–168°. Since the two dibromopyromucic acids and unaltered pyromucic acid were formed from a product containing equal molecules of ethyl pyromucate and bromine, we were led to the conclusion that no dibromide had been formed under the conditions chosen, and that the supposed dibromide was in fact only a mixture of unaltered pyromucic ether with its tetrabromide. Since at ordinary temperatures quantities of hydrobromic acid were evolved on mixing the pyromucic ether with bromine,† (a fact not mentioned by Schiff and Tassinari or by Canzoneri and Oliveri,) it was evident that the monobromopyromucic acid which appeared among the products could readily have been formed by direct substitution. On submitting the mixture of equal molecules of pyromucic ether and bromine to fractional distillation in vacuo, it was easy to isolate among the more volatile products the ethyl ether of  $\delta$ -monobromopyromucic acid and ethyl pyromucate, melting at 34–35°. The ethyl monobromopyromucate still contained ethyl pyromucate, since the percentage of bromine which we found was much too low.

0.1890 grm. substance gave 0.1487 grm. AgBr.

	Calculated for $(C_8H_2)(C_8H_2BrO_8)$ .	Found.
Br	36.54	33.49

The acid obtained from the ether, when recrystallized from water, melted at 182–183°.

\* Gazzetta Chimica, xiv. 173.

† The evolution of hydrobromic acid was invariably observed, although we varied in many ways the conditions under which the reaction took place. In addition to the glacial acetic acid recommended by Schiff and Tassinari as a solvent, we tried carbonic disulphide and chloroform with the same results.

ACTION OF ALCOHOLIC SODIC HYDRATE UPON PYROMUCIC  
TETRABROMIDE.

By acting upon pyromucic tetrabromide with an alcoholic solution of potassic hydrate, Toennies obtained a dibrompyromucic acid melting at 186°. In the preliminary paper already referred to,\* he gives no description of the conditions under which the decomposition was effected, and, as far as we are aware, he has never published any more extended account of his work.

The pyromucic tetrabromide we prepared according to his directions by exposing pyromucic acid to the vapors of bromine. The bromine was quite rapidly absorbed, and the acid was converted into a voluminous porous mass from which the excess of bromine could readily be expelled by a short exposure to the air. The formation of this addition product, however, was not the only reaction which took place, since hydrobromic acid was invariably evolved in no insignificant quantities, and the product therefore contained also  $\delta$ -monobrompyromucic acid and its tetrabromide. For the purification of the pyromucic tetrabromide we have found glacial acetic acid (99.5 per cent) more advantageous than the mixture of ligroin and ether recommended by Toennies.

Since the purification of large quantities of the tetrabromide was at best a matter of difficulty, we have used in our work the crude product more especially since the isolation of the products formed from it presented no greater difficulties. Instead of using an alcoholic solution of potassic hydrate for its decomposition, we have taken sodic hydrate, since the sodium salts of the acids formed seemed to be somewhat less soluble in alcohol than the potassium salts. We have found that the best results may be obtained by using a decided excess of a concentrated solution of the alkaline hydrate, taking care that the temperature does not rise above 25°. The greater part of the sodium salts formed separates at once, and may be filtered off upon the pump. The sodium salt dissolved in water and acidified with hydrochloric acid yields an acid, usually more or less colored, which is readily soluble in cold water, more readily in hot, and whose melting-point is quite constant (136–138°). This consists essentially of a mixture of two isomeric dibrompyromucic acids, although it frequently contains small quantities of  $\delta$ -monobrompyromucic and tribrompyromucic acids. The aqueous solution filtered from these acids contains also oxalic acid.

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\* Berichte der deutschen chem. Gesellsch., xi. 1086.

Although we have not found it possible to separate these acids directly by fractional crystallization, they may be separated by means of their calcium salts. While we have found it easy to prepare in this way small quantities of the pure acids, the complete separation of large quantities of the acids involves a very considerable amount of time and labor. We have found it most convenient to dissolve the mixed acids in ammoniac hydrate, and to add calcic chloride to the dilute solution (1:30). A very sparingly soluble crystalline calcium salt is thus thrown down, which contains chiefly one of the two dibromopyromucic acids, while the calcium salts of the other acids remain in solution. The sparingly soluble calcium salt may be purified by recrystallization from boiling water, or the acid may be set free, the calcium salt reprecipitated, and the operation repeated until the melting-point of the acid is found to be 164–166°. The solution containing the more soluble calcium salts is acidified, and the acids thus obtained are separated by recrystallization from boiling water. The tribromopyromucic acid is almost insoluble in water, while the  $\delta$ -monobromopyromucic acid, though but slightly more soluble in cold water than the dibromopyromucic acid, is present in such small quantity that its removal is a matter of little difficulty. When the melting-point of the dibromopyromucic acid has been raised to 184° by recrystallization from water, its further purification is effected by washing or recrystallizing from benzol. The acid whose calcium salt is more sparingly soluble in water, and which, as we shall afterward show, is the  $\beta\delta$ -dibromopyromucic acid, melts at 167–168°, while the isomeric  $\beta\gamma$ -dibromopyromucic acid, whose calcium salt is more readily soluble, melts at 191–192°. Although we have made many attempts to control at will the quantities of the two dibromopyromucic acids formed, we have as yet met with no success. The yield of the mixed acids was far from satisfactory, and amounted to but from thirty-four to thirty-eight per cent of that theoretically required. The difficulties in the way of complete separation of the two acids make it impossible for us to give the precise ratio between the amounts of the two isomers found. While we have usually obtained nearly twice as much of the low-melting acid as of the high, we are inclined to think that the original mixture contained them in nearly equal quantities.

The alcoholic filtrate from the sodium salts contained, beside small quantities of these salts in solution, considerable quantities of sodic  $\delta$ -monobromopyromucate. When diluted with water, it became turbid, with the separation of a small quantity of a colorless oil. In order to determine its nature, we distilled the filtrate with steam and precipi-

tated the alcoholic distillate by the further addition of water. The oil which was thus thrown down was dried with calcic chloride and distilled under diminished pressure. The wide range in boiling-point ( $60\text{--}130^\circ$  at 17 mm.) which we then observed showed its nature to be tolerably complex. After repeated distillations, we were able to isolate one fraction (A) boiling between  $59^\circ$  and  $69^\circ$  under 17 mm. pressure, and a somewhat larger fraction boiling at  $94\text{--}99^\circ$  under a pressure of 17 mm. This second fraction partially solidified on standing, and the crystals (B) were separated from the oily mother-liquor (C) by filtration. With a second larger quantity of the alcoholic filtrate subsequently obtained we adopted a somewhat different method. We precipitated the excess of sodic hydrate by carbonic dioxide, distilled the alcoholic filtrate, and precipitated the distillate with water. After several distillations in vacuo, we obtained one fraction (D) boiling at  $57\text{--}62^\circ$  under a pressure of 20 mm., a second (E) boiling at  $61\text{--}68^\circ$  under a pressure of 19 mm., and a third boiling at  $98\text{--}102^\circ$  under a pressure of 19 mm., which as before partially solidified on standing, and the crystals (F) were separated by filtration from the mother-liquor (G). The fractions boiling between  $68^\circ$  and  $98^\circ$  were insignificant in quantity.

The lower boiling fractions proved, on analysis, to contain a percentage of bromine, agreeing closely with that required by the formula  $\text{C}_4\text{H}_2\text{Br}_2\text{O}$ .

- I. 0.2444 grm. of substance (A) gave 0.4060 grm. AgBr.
- II. 0.2503 grm. of substance (A) gave 0.4160 grm. AgBr.
- III. 0.3593 grm. of substance (D) gave 0.5959 grm. AgBr.
- IV. 0.2559 grm. of substance (E) gave 0.4284 grm. AgBr.
- V. 0.3416 grm. of substance (E) gave 0.5715 grm. AgBr.

	Calculated for $\text{C}_4\text{H}_2\text{Br}_2\text{O}$ .	I.	II.	Found. III.	IV.	V.
Br	70.79	70.69	70.74	70.58	71.25	71.19

The great variation in boiling-point with this slight variation in percentage composition renders it probable that the oil contained two isomeric dibromfurfurans. The fraction boiling at  $61\text{--}68^\circ$ , after standing for a few days, was unfortunately largely converted into an amorphous black solid; the lower fraction remained unaltered. When the lower fraction was treated with bromine, hydrobromic acid was evolved even at ordinary temperatures, so that no corresponding addition product could be prepared, and we have hitherto been unable to obtain

by oxidation any products which would enable us to draw any conclusion as to its constitution.

The solid which separated from the higher fractions, on cooling when recrystallized from alcohol, formed broad flattened needles which melted at  $77^{\circ}$ . It was readily soluble in alcohol, ether, chloroform, or benzol, more sparingly soluble in carbonic disulphide or ligroin. The percentage of bromine which the substance contained agreed precisely with that required by the formula  $C_4H_8BrO_2$ . While the combustion of the substance gave a percentage of carbon materially greater than that which this formula requires, it seemed to us to leave no doubt of the composition of the substance. We were therefore unwilling to sacrifice the small amount of the substance which we had left in order to make a second combustion.

- I. 0.5251 grm. of substance (F) gave 0.5742 grm.  $CO_2$  and 0.0949 grm.  $H_2O$ .
- II. 0.1523 grm. of substance (B) gave 0.1758 grm. AgBr.
- III. 0.2186 grm. of substance (F) gave 0.2527 grm. AgBr.

	Calculated for $C_4H_8BrO_2$	I.	Found. II.	III.
C	29.44	29.82		
H	1.84	2.01		
Br	49.09		49.14	49.19

The small amount of this substance at our disposal — we obtained but three grammes of the crude product from 2.6 kilogrammes of pyromucic tetrabromide — has made it impossible for us to submit it to any very extended investigation. In aqueous solution it reduces silver oxide, and at the same time argentic bromide is formed. We were unable, however, to isolate any definite products of the oxidation. With nitric acid, apparently nothing but oxalic acid was formed. It was unaffected by dry bromine, but when treated with bromine and water it was converted into an amorphous substance insoluble or sparingly soluble in all common solvents. It was readily decomposed by aqueous alkalis. The solution had a bright yellow color, and contained potassic bromide, but we have been unable to determine the products resulting from the reaction.

This ready decomposition in alkaline solution makes it probable that it was formed during the process of distillation, although it is perhaps possible that the small quantity which we were able to obtain was only that portion which chanced to escape decomposition in the

original alkaline solution. It will be noticed that this substance is isomeric with a product obtained by Limpricht by the action of bromine upon pyromucic acid under conditions which he was unable to fix precisely. The higher melting-point,  $84^{\circ}$ , and the fact that it was unaffected by an alcoholic solution of potassic hydrate at  $180^{\circ}$ , establish with sufficient precision their essential difference.

The higher boiling fractions from which this crystalline substance had been separated as completely as possible gave, on analysis, a percentage of bromine, which showed that they consisted mainly of a tribromfurfuran. The difficulty of removing completely, by distillation or by freezing, the solid constituent, sufficiently explains the low percentages of bromine we have obtained.

- I. 0.2312 grm. of substance (C) gave 0.4130 grm. AgBr.
- II. 0.3253 grm. of substance (C) gave 0.5855 grm. AgBr.
- III. 0.2897 grm. of substance (G) gave 0.5246 grm. AgBr.
- IV. 0.2291 grm. of substance (G) gave 0.4130 grm. AgBr.

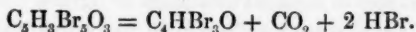
Br	Calculated for	Found.			
	$C_5HBr_3O$ .	I.	II.	III.	IV.
	78.68	76.03	76.61	77.05	76.74

This tribromfurfuran, when treated with bromine, gave off at ordinary temperatures clouds of hydrobromic acid, so that the corresponding addition product could not be prepared. We have also been unable as yet to obtain any definite oxidation products containing four carbon atoms.

The formation of dibromfurfuran from pyromucic tetrabromide evidently takes place according to the equation,



The tribromfurfuran must, of necessity, be formed from the monobrompyromucic tetrabromide which the crude pyromucic tetrabromide contains, —



#### $\beta$ -DIBROMPYROMUCIC ACID.

This acid is formed, as has already been explained, together with the isomeric  $\beta$ -dibrompyromucic acid, by the action of an alcoholic solution of sodic hydrate upon pyromucic tetrabromide. It may, how-

ever, be more conveniently, if not more economically, prepared by the direct action of bromine upon pyromucic acid. The reaction is apparently quite complex, a large excess of bromine is required, and the product is small compared with that theoretically required. Pyromucic acid is treated with about three molecules of bromine, and heated on the water bath with reverse cooler, until the evolution of hydrobromic acid is over. There remains, then, in the flask a red viscous oil which contains  $\beta\delta$ -dibrompyromucyl bromide with a small amount of  $\delta$ -monobrompyromucyl bromide, dibrommaleic acid or its anhydride, and other products not yet more exactly determined. This oil is washed with cold water to remove the more soluble products, and is then boiled with water until the acid bromides are converted into the acids. The separation of the dibrompyromucic from the monobrompyromucic acid with which it is mixed may be most conveniently effected by precipitating its barium salt from an ammoniacal solution by the addition of baric chloride, and repeating the operation until a product melting at  $165$ - $166^\circ$  is obtained. By subsequent recrystallization from hot water and from benzol the melting-point may then be raised to  $167$ - $168^\circ$ .

The acid thus purified gave, on analysis, the following results:—

- I. 0.5370 grm. substance gave 0.4379 grm.  $\text{CO}_2$  and 0.0390 grm.  $\text{H}_2\text{O}$ .
- II. 0.2251 grm. substance gave 0.3125 grm. AgBr.
- III. 0.1665 grm. substance gave 0.2323 grm. AgBr.

	Calculated for $\text{C}_6\text{H}_2\text{Br}_2\text{O}_6$	I.	Found. II.	III.
C	22.22	22.24		
H	0.74	0.81		
Br	59.26		59.09	59.39

The  $\beta\delta$ -dibrompyromucic acid is readily soluble in alcohol or ether, freely soluble in boiling chloroform, quite readily soluble in benzol, but sparingly soluble in carbonic disulphide or ligroin. It is sparingly soluble in cold water, quite readily soluble in boiling water, and crystallizes on cooling in small oblique prisms, which, however, usually appear in characteristic twinned forms.

The solubility of the acid in water at ordinary temperatures we determined by neutralizing with baric carbonate the saturated solution, and determining by precipitation with sulphuric acid the amount of barium dissolved.

- I. 38.3346 grm. of a solution saturated at 20° gave 0.0462 grm.  $\text{BaSO}_4$ .  
 II. 38.3935 grm. of a solution saturated at 20° gave 0.0464 grm.  $\text{BaSO}_4$ .

According to these determinations the aqueous solution of the acid saturated at 20° contained the following percentages:—

I.	II.
0.28	0.28

*Baric β̄-Dibromopyromucate*,  $\text{Ba}(\text{C}_5\text{HBr}_2\text{O}_3)_2 \cdot 4 \text{H}_2\text{O}$ .—The barium salt we prepared by neutralizing a boiling aqueous solution of the acid with baric carbonate. After recrystallization from boiling water, it formed fine branching needles. The air-dried salt contained four molecules of water, three of which it lost over sulphuric acid.

- I. 1.4800 grm. of air-dried salt lost 0.1117 grm.  $\text{H}_2\text{O}$  over sulphuric acid, and in addition 0.0324 grm.  $\text{H}_2\text{O}$  at 110°.  
 II. 2.1113 grm. of the air-dried salt lost at 110° 0.2030 grm.  $\text{H}_2\text{O}$ .

	Calculated for $\text{Ba}(\text{C}_5\text{HBr}_2\text{O}_3)_2 \cdot 4 \text{H}_2\text{O}$ .	Found.	
		I.	II.
3 $\text{H}_2\text{O}$	7.23	7.54	
4 $\text{H}_2\text{O}$	9.64	9.74	9.60

- I. 0.4109 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1415 grm.  $\text{BaSO}_4$ .  
 II. 0.7780 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.2666 grm.  $\text{BaSO}_4$ .

	Calculated for $\text{Ba}(\text{C}_5\text{HBr}_2\text{O}_3)_2$	Found.	
		I.	II.
Ba	20.30	20.24	20.14

The solubility of the salt in cold water we determined by precipitating the saturated solution with sulphuric acid.

- I. 38.7621 grm. of a solution saturated at 16° gave 0.0132 grm.  $\text{BaSO}_4$ .  
 II. 36.2526 grm. of a solution saturated at 16° gave 0.0129 grm.  $\text{BaSO}_4$ .

The aqueous solution saturated at 16° therefore contained the following percentages of the anhydrous salt:—

I.	II.
0.10	0.10

*Calcic  $\beta\delta$ -Dibromopyromucate*,  $\text{Ca}(\text{C}_5\text{HBr}_2\text{O}_3)_2 \cdot 3 \text{H}_2\text{O}$ . — On neutralizing a boiling aqueous solution of the acid with calcic carbonate, we obtained the calcium salt in small clustered prisms, which we purified by recrystallization from boiling water. The air-dried salt contained three molecules of water, one of which it lost over sulphuric acid.

- I. 1.1374 grm. of air-dried salt lost over sulphuric acid 0.0275 grm.  $\text{H}_2\text{O}$ , and in addition 0.0706 grm.  $\text{H}_2\text{O}$  at  $110^\circ$ .  
 II. 1.4733 grm. of the air-dried salt lost at  $112^\circ$  0.0984 grm.  $\text{H}_2\text{O}$ .

	Calculated for $\text{Ca}(\text{C}_5\text{HBr}_2\text{O}_3)_2 \cdot 3 \text{H}_2\text{O}$ .	Found.	
		I.	II.
$\text{H}_2\text{O}$	2.85	2.42	
3 $\text{H}_2\text{O}$	8.56	8.63	8.36

- I. 0.4709 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1107 grm.  $\text{CaSO}_4$ .  
 II. 0.6026 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1387 grm.  $\text{CaSO}_4$ .

	Calculated for $\text{Ca}(\text{C}_5\text{HBr}_2\text{O}_3)_2$ .	Found.	
		I.	II.
Ca	6.92	6.91	6.77

The solubility of the salt in cold water we determined by evaporation and ignition with sulphuric acid.

- I. 39.5194 grm. of a solution saturated at  $17^\circ$  gave 0.0288 grm.  $\text{CaSO}_4$ .  
 II. 50.3735 grm. of a solution saturated at  $17^\circ$  gave 0.0344 grm.  $\text{CaSO}_4$ .

The aqueous solution saturated at  $17^\circ$  therefore contained the following percentages of the anhydrous salt:—

I.	II.
0.31	0.29

*Argentio  $\beta\delta$ -Dibromopyromucate*,  $\text{AgC}_5\text{HBr}_2\text{O}_3$ . — From an aqueous solution of the acid argentic nitrate precipitates the silver salt in the form of fine clustered needles, which may be recrystallized from hot water without essential decomposition. For analysis we prepared it by precipitating a solution of argentic nitrate with a solution of the acid neutralized by ammonic hydrate.

0.3275 grm. of the salt dried over sulphuric acid gave 0.1646 grm.  $\text{AgBr}$ .

	Calculated for $\text{AgC}_5\text{HBr}_2\text{O}_3$ .	Found.
Ag	28.65	28.87

*Sodic  $\beta\delta$ -Dibrompyromucate*,  $\text{NaC}_5\text{HBr}_2\text{O}_3 \cdot 2 \text{H}_2\text{O}$ . — The sodium salt we prepared by dissolving the acid in a solution of sodic carbonate, and subsequent recrystallization from water. It formed short needles, which were not very soluble in cold water, and which, when air-dried, contained two molecules of water.

- I. 1.0207 grm. of the air-dried salt lost at  $122^\circ$  0.1095 grm.  $\text{H}_2\text{O}$ .  
 II. 1.1177 grm. of the air-dried salt lost at  $122^\circ$  0.1201 grm.  $\text{H}_2\text{O}$ .

	Calculated for	Found.	
	$\text{NaC}_5\text{HBr}_2\text{O}_3 \cdot 2 \text{H}_2\text{O}$ .	I.	II.
$\text{H}_2\text{O}$	10.97	10.73	10.75

- I. 0.5364 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1284 grm.  $\text{Na}_2\text{SO}_4$ .  
 II. 0.5492 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1314 grm.  $\text{Na}_2\text{SO}_4$ .

	Calculated for	Found.	
	$\text{NaC}_5\text{HBr}_2\text{O}_3$ .	I.	II.
Na	7.88	7.76	7.75

*Potassic  $\beta\delta$ -Dibrompyromucate*,  $\text{KC}_5\text{HBr}_2\text{O}_3$ . — The potassium salt prepared by dissolving the acid in a dilute solution of potassic carbonate, and recrystallizing the product thus obtained from water, crystallized in long concentrically grouped needles, which proved to be anhydrous.

- I. 0.5986 grm. of the salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1691 grm.  $\text{K}_2\text{SO}_4$ .  
 II. 0.6018 grm. of the salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1680 grm.  $\text{K}_2\text{SO}_4$ .

	Calculated for	Found.	
	$\text{KC}_5\text{HBr}_2\text{O}_3$ .	I.	II.
K	12.69	12.69	12.53

*Ethyl  $\beta\delta$ -Dibrompyromucate*,  $(\text{C}_2\text{H}_5)\text{C}_5\text{HBr}_2\text{O}_3$ . — The ethyl ether we have made by the action of ethyl iodide upon the silver salt of the acid, and also by heating an alcoholic solution of the acid with concentrated sulphuric acid. By the latter method we have obtained a good yield by dissolving five parts of the acid in an equal weight of absolute alcohol, adding three parts of concentrated sulphuric acid, and warming for several hours at  $100^\circ$ . The product precipitated by the addition of water we washed with a dilute solution of sodic carbonate and purified by recrystallization from alcohol. It crystallized in small,

flat, clustered prisms, which melted at 57–58°, and boiled with decided decomposition at 271–272° (mercury column completely in vapor), under a pressure of 765 mm. The ether has a pleasant, fragrant odor, not unlike that of ethyl pyromucate. It is readily soluble in ether, chloroform, benzol, or ligroin, somewhat less soluble in carbonic disulphide. It is readily soluble in hot alcohol, much more sparingly soluble in cold. The ether used in Analysis II. was made from the silver salt.

- I. 0.1524 grm. substance gave 0.1927 grm. AgBr.  
 II. 0.2024 grm. substance gave 0.2556 grm. AgBr.

Br	Calculated for (C <sub>5</sub> H <sub>5</sub> )C <sub>5</sub> HBr <sub>3</sub> O <sub>2</sub>	Found.	
		I.	II.
	53.69	53.83	53.74

*βδ-Dibromopyromucyl Bromide*, C<sub>5</sub>HBr<sub>3</sub>O<sub>2</sub>. — It has already been said that *βδ*-dibromopyromucyl bromide is formed by the action of dry bromine upon pyromucic acid. In order to isolate it, we submitted the viscous oil which was thus formed to fractional distillation in vacuo. After repeated distillations a fraction was isolated, boiling at 149–155° under a pressure of 24 mm., most of which passed over between 153° and 155°. This fraction, on standing over sulphuric acid, gradually solidified, and the solid thus obtained could readily be purified by recrystallization from ligroin. On heating with water it formed *βδ*-dibromopyromucic acid; with alcohol, it gave the ether melting at 56–57°; and on analysis it gave the percentage of bromine required by the formula C<sub>5</sub>HBr<sub>3</sub>O<sub>2</sub>. Analysis III. was made with material prepared from the crude product by crystallization alone without previous distillation.

- I. 0.2214 grm. substance gave 0.3752 grm. AgBr.  
 II. 0.1876 grm. substance gave 0.3180 grm. AgBr.  
 III. 0.2152 grm. substance gave 0.3640 grm. AgBr.

Br	Calculated for C <sub>5</sub> HBr <sub>3</sub> O <sub>2</sub>	Found.		
		I.	II.	III.
	72.07	72.11	72.14	71.99

The *βδ*-dibromopyromucyl bromide crystallizes in small compact prisms which melt at 45–46°. It is readily soluble in alcohol, ether, chloroform, or benzol, somewhat less soluble in ligroin. It is slowly attacked by cold water, more readily by hot.

From the lower fractions there separated, on standing, prismatic crystals, which, from their behavior and from their melting-point

(114–115°), were shown to be dibrommaleic anhydride. In confirmation we prepared from the aqueous solution obtained by washing the crude product with cold water considerable quantities of baric dibrommaleate, which was identified by analysis.

0.5423 grm. of the air-dried salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.2853 grm.  $\text{BaSO}_4$ .

	Calculated for $\text{BaC}_4\text{Br}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ .	Found.
Ba	30.78	30.93

Since the most volatile portions of the oil gave with water  $\delta$ -monobrompyromucic acid, it contained doubtless the corresponding monobrompyromucyl bromide. The quantity, however, appeared to be so small that we made no attempt to isolate it.

*$\beta\delta$ -Dibrompyromucamide*,  $\text{C}_5\text{HBr}_2\text{O}_2\text{NH}_2$ .—Concentrated aqueous ammonia acts but slowly upon the ethyl ether of  $\beta\delta$ -dibrompyromucic acid, and even after long standing the decomposition is imperfect. The amide may readily be made from the bromide just described by the action of aqueous ammonia, and may be purified by recrystallization from hot water. Thus prepared, it forms long silky needles which melt at 175–176°. It is readily soluble in alcohol, quite readily soluble in ether, chloroform, or hot benzol, and almost insoluble in carbonic disulphide or ligroin. It is sparingly soluble in cold water, but freely soluble in hot water.

0.9102 grm. substance gave 44.5 c.c. moist nitrogen at 14.5° and under a pressure of 722 mm.

	Calculated for $\text{C}_5\text{HBr}_2\text{O}_2\text{NH}_2$ .	Found.
N	5.20	5.31

#### *Action of Bromine and Water.*

We found that the  $\beta\delta$ -dibrompyromucic acid was rather slowly attacked by bromine in aqueous solution, and the reaction appeared to be essentially the same whether the bromine was added rapidly or slowly. We therefore suspended the acid in water, and added at once rather more than two molecules of bromine, taking care to prevent any decided rise of temperature. Carbonic dioxide was slowly evolved, and the red oil which was at first formed gradually solidified. The product was then pressed with filter-paper, and recrystallized from boiling ligroin. Treatment with bone-black was usually necessary in order to obtain a colorless product. The substance thus

prepared was very readily soluble in alcohol, ether, chloroform, carbonic disulphide, or benzol, more sparingly soluble in ligroin, from which it crystallized in long lustrous prisms which melted at 55–56°. By the slow evaporation of the solution in ligroin quite large and well-developed individuals could be obtained. The substance dried over sulphuric acid gave on analysis the following results:—

- I. 0.9663 grm. substance gave 0.5285 grm. CO<sub>2</sub> and 0.0300 grm. H<sub>2</sub>O.  
 II. 0.2053 grm. substance gave 0.3594 grm. AgBr.  
 III. 0.2344 grm. substance gave 0.4109 grm. AgBr.

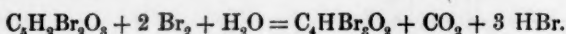
	Calculated for C <sub>6</sub> HBr <sub>3</sub> O <sub>4</sub> .	I.	Found. II.	III.
C	14.95	14.91		
H	0.31	0.35		
Br	74.76		74.50	74.61

When boiled with water this substance was gradually decomposed, and the aqueous solution then appeared to contain a mixture of dibromsuccinic, monobromfumaric, and monobrommaleic acid, as far as could be determined from the melting-points and other physical properties of the products obtained by evaporation and recrystallization. Since we thought it not improbable that the dibromsuccinic and monobromfumaric acids had been formed from the monobrommaleic acid by the action of the hydrobromic acid formed in the reaction, we decomposed the substance by heating it with a dilute solution of potassic hydrate, added hydrochloric acid in quantity just sufficient to set the organic acid free, extracted with ether, and recrystallized from water the residue left upon evaporation of the ether. In this way we obtained a homogeneous product which melted at 126–127°, and which gave on analysis the percentage of bromine required by monobrommaleic acid.

0.2099 grm. substance gave 0.2013 grm. AgBr.

	Calculated for C <sub>4</sub> H <sub>3</sub> BrO <sub>4</sub> .	Found.
Br	41.03	40.82

The chief product of the action of aqueous bromine upon βδ-dibrompyromucic acid was therefore monobrommaleyl bromide formed according to the equation,



We have obtained usually about seventy per cent of the theoretical yield of monobrommaleyl bromide, and have been able to isolate no other products of the reaction except such as would naturally result from its decomposition with water.

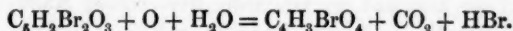
#### *Action of Nitric Acid.*

The  $\beta\delta$ -dibrompyromucic acid is readily oxidized, with evolution of carbonic dioxide, by boiling even with dilute nitric acid. We have found two parts of strong nitric acid (sp. gr. 1.42), diluted with ten parts of water, sufficient for the complete oxidation of one part of the acid. After the reaction was ended, we extracted the solution with ether and crystallized from water the product obtained by the evaporation of the ether. This product appeared to contain nothing but an acid melting at  $174-175^\circ$ , which on analysis gave the percentage of bromine required by monobromfumaric acid.

0.2254 grm. substance gave 0.2186 grm. AgBr.

	Calculated for $C_4H_3BrO_4$ .	Found.
Br	41.03	41.28

Since we have already shown that the product formed by the action of aqueous bromine is a derivative of monobrommaleic acid, we have not hesitated to assume that the first product of the oxidation with nitric acid also is monobrommaleic acid, and that this is converted into monobromfumaric acid by the continued boiling with nitric acid. The reaction may be written,



#### $\beta\gamma$ -DIBROMPYROMUCIC ACID.

The formation of  $\beta\gamma$ -dibrompyromucic acid from the pyromucic tetrabromide has already been described, and we have not been able to find any other method for its preparation. For analysis, the acid was recrystallized several times from water, and finally from benzol.

I. 0.6274 grm. substance gave 0.5065 grm.  $CO_2$  and 0.0445 grm.  $H_2O$ .

II. 0.2165 grm. substance gave 0.3019 grm. AgBr.

III. 0.2225 grm. substance gave 0.3106 grm. AgBr.

	Calculated for $C_5H_2Br_2O_8$	I	Found. II.	III.
C	22.22	22.02		
H	0.74	0.79		
Br	59.26		59.33	59.40

The  $\beta\gamma$ -dibromopyromucic acid crystallizes from benzol in short clustered prisms, from water in voluminous feather-like forms. It is readily soluble in ether or alcohol, quite readily soluble in boiling benzol or chloroform, and but sparingly soluble in carbonic disulphide or ligroin. It is rather sparingly soluble even in hot water, and still less soluble in cold water. The solubility of the acid in water at ordinary temperatures we determined by boiling the saturated solution with baric carbonate and precipitating with sulphuric acid the barium dissolved.

I. 53.3668 grm. of a solution saturated at  $20^\circ$  gave 0.0481 grm.  $BaSO_4$ .

II. 50.6792 grm. of a solution saturated at  $20^\circ$  gave 0.0477 grm.  $BaSO_4$ .

The aqueous solution saturated at  $20^\circ$  therefore contained the following percentages of the acid:—

I.	II.
0.21	0.22

*Baric  $\beta\gamma$ -Dibromopyromucate*,  $Ba(C_5HBr_2O_8)_2 \cdot 3H_2O$ .—The barium salt we made by precipitating with baric chloride a dilute ammoniacal solution of the acid, and recrystallizing from boiling water the salt thus precipitated. It formed irregular radiating flattened needles which effloresced over sulphuric acid, but which contained three molecules of water when dried by exposure to the air.

I. 1.6173 grm. of the air-dried salt lost at  $150^\circ$  0.1226 grm.  $H_2O$ .

II. 1.1994 grm. of the air-dried salt lost at  $130^\circ$  0.0847 grm.  $H_2O$ .

	Calculated for $Ba(C_5HBr_2O_8)_2 \cdot 3H_2O$	Found. I	II.
$H_2O$	7.41	7.58	7.06

I. 1.4947 grm. of the anhydrous salt gave on ignition with  $H_2SO_4$  0.5197 grm.  $BaSO_4$ .

II. 0.4555 grm. of the anhydrous salt gave on ignition with  $H_2SO_4$  0.1544 grm.  $BaSO_4$ .

	Calculated for $\text{Ba}(\text{C}_5\text{HBr}_2\text{O}_3)_2$	Found.	
		I.	II.
Ba	20.30	20.44	19.93

The solubility of the salt in cold water we determined by precipitating the saturated solution with sulphuric acid.

- I. 41.9064 grm. of a solution saturated at  $20^\circ$  gave 0.0521 grm.  $\text{BaSO}_4$ .  
 II. 37.7244 grm. of a solution saturated at  $20^\circ$  gave 0.0449 grm.  $\text{BaSO}_4$ .

The aqueous solution saturated at  $20^\circ$  therefore contained the following percentages of the anhydrous salt:—

I.	II.
0.36	0.34

*Calcic  $\beta$ -Dibrompyromucate*,  $\text{Ca}(\text{C}_5\text{HBr}_2\text{O}_3)_2 \cdot 5 \text{H}_2\text{O}$ .—The calcium salt we made by boiling the acid with water and adding calcic carbonate. The salt recrystallized from boiling water formed concentrically grouped needles, which effloresced slowly in the air, rapidly over sulphuric acid.

- I. 1.7504 grm. of the salt lost at  $120^\circ$  0.2330 grm.  $\text{H}_2\text{O}$ .  
 II. 2.4934 grm. of the salt lost at  $120^\circ$  0.3300 grm.  $\text{H}_2\text{O}$ .

	Calculated for $\text{Ca}(\text{C}_5\text{HBr}_2\text{O}_3)_2 \cdot 5 \text{H}_2\text{O}$	Found.	
		I.	II.
$\text{H}_2\text{O}$	13.47	13.31	13.23

- I. 0.5620 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1301 grm.  $\text{CaSO}_4$ .  
 II. 0.8701 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.2011 grm.  $\text{CaSO}_4$ .

	Calculated for $\text{Ca}(\text{C}_5\text{HBr}_2\text{O}_3)_2$	Found.	
		I.	II.
Ca	6.92	6.81	6.80

The solubility of the salt in water at ordinary temperatures we determined by precipitating a saturated solution with ammonic oxalate, and igniting the calcic oxalate thus obtained with sulphuric acid.

- I. 20.5686 grm. of a solution saturated at  $20^\circ$  gave 0.0561 grm.  $\text{CaSO}_4$ .  
 II. 19.7985 grm. of a solution saturated at  $20^\circ$  gave 0.0538 grm.  $\text{CaSO}_4$ .

The solution saturated at 20° therefore contained the following percentages of the anhydrous salt:—

I.	II.
1.16	1.15

*Argentio βγ-Dibrompyromucate*,  $\text{AgC}_5\text{HBr}_2\text{O}_3$ .— From an aqueous solution of the acid argentic nitrate precipitates the silver salt in the form of minute clustered needles, which dissolve without essential decomposition on heating the solution. For analysis we prepared it by precipitating with argentic nitrate a neutral solution of the acid in dilute ammoniac hydrate.

0.2584 grm. of the salt gave on precipitation with  $\text{HBr}$  0.1297 grm.  $\text{AgBr}$ .

	Calculated for $\text{AgC}_5\text{HBr}_2\text{O}_3$ .	Found.
Ag	28.65	28.83

*Sodio βγ-Dibrompyromucate*,  $\text{NaC}_5\text{HBr}_2\text{O}_3 \cdot 2 \text{H}_2\text{O}$ .— The sodium salt we prepared by dissolving the acid in a solution of sodic carbonate and recrystallizing from water the salt thus obtained. It formed fine silky needles, which were not very soluble in cold water. The air-dried salt contained two molecules of water.

- I. 2.0032 grm. of the air-dried salt lost at 119° 0.2192 grm.  $\text{H}_2\text{O}$ .  
 II. 1.7440 grm. of the air-dried salt lost at 119° 0.1925 grm.  $\text{H}_2\text{O}$ .

	Calculated for $\text{NaC}_5\text{HBr}_2\text{O}_3 \cdot 2 \text{H}_2\text{O}$ .	Found.	
$\text{H}_2\text{O}$	10.97	I.	II.
		10.94	11.04

- I. 0.6162 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1502 grm.  $\text{Na}_2\text{SO}_4$ .  
 II. 0.6275 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1506 grm.  $\text{Na}_2\text{SO}_4$ .

	Calculated for $\text{NaC}_5\text{HBr}_2\text{O}_3$ .	Found.	
Na	7.88	I.	II.
		7.90	7.78

*Potassio βγ-Dibrompyromucate*,  $\text{KC}_5\text{HBr}_2\text{O}_3$ .— The potassium salt made by neutralizing the acid with potassic carbonate crystallized in flat clustered prisms, which were not very soluble in cold water and were anhydrous.

- I. 0.5082 grm. of the salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1390 grm.  $\text{K}_2\text{SO}_4$ .

II. 0.9303 grm. of the salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.2603 grm.  $\text{K}_2\text{SO}_4$ .

	Calculated for $\text{KC}_5\text{HBr}_2\text{O}_3$ .	Found.	
		I.	II.
K	12.69	12.57	12.56

*Ethyl  $\beta\gamma$ -Dibrompyromucate*,  $(\text{C}_2\text{H}_5)_2\text{C}_5\text{HBr}_2\text{O}_3$ . — The ethyl ether we have prepared by the action of ethyl iodide upon the silver salt of the acid, and also by heating the acid in alcoholic solution with concentrated sulphuric acid. For its preparation by the latter method we used the same proportions which we had already found advantageous in the case of the  $\beta\delta$ -dibrompyromucic acid; namely, five parts of the acid, five of absolute alcohol, and three of concentrated sulphuric acid. The reaction was completed in a few hours at  $100^\circ$ , and the ether was precipitated with water, washed with a dilute solution of sodic carbonate, and recrystallized from alcohol. Thus prepared, it formed fine silky needles which melted at  $67$ – $68^\circ$ . Its odor recalled at the same time ethyl pyromucate and anise. It is readily soluble in ether, chloroform, benzol, carbonic disulphide, ligroin, or hot alcohol, sparingly soluble in cold alcohol. The material used in Analysis II. was made from the silver salt by the action of ethyl iodide.

- I. 0.2193 grm. substance gave 0.2777 grm.  $\text{AgBr}$ .  
 II. 0.1497 grm. substance gave 0.1886 grm.  $\text{AgBr}$ .

	Calculated for $(\text{C}_2\text{H}_5)_2\text{C}_5\text{HBr}_2\text{O}_3$ .	Found.	
		I.	II.
Br	53.69	53.91	53.62

*$\beta\gamma$ -Dibrompyromucamide*,  $\text{C}_5\text{HBr}_2\text{O}_2\text{NH}_2$ . — Since concentrated aqueous ammonia acted but slowly upon the ethyl  $\beta\gamma$ -dibrompyromucate in the cold, we heated the mixture in sealed tubes at  $100^\circ$  for several hours. The resulting amide we purified by recrystallization from dilute alcohol. It crystallized from alcohol in fine needles, which melted at  $195$ – $196^\circ$ . It was readily soluble in alcohol, quite sparingly soluble in ether, chloroform, or benzol, and almost insoluble in carbonic disulphide or ligroin. Even in boiling water it was but sparingly soluble.

0.9791 grm. of substance gave 47.0 c.c. of moist nitrogen at  $23^\circ$  under a pressure of 739 mm.

	Calculated for $\text{C}_5\text{HBr}_2\text{O}_2\text{NH}_2$ .	Found.
N	5.20	5.38

The  $\beta$ -dibromopyromucic acid appears to be incapable of forming an addition product with bromine. When the acid is exposed to an atmosphere of bromine at ordinary temperatures, hydrobromic acid is evolved, and tribromopyromucic acid is formed. This we identified by its melting-point, 218–219°, and by its other physical properties.

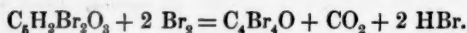
*Action of Bromine and Water.*

Toennies obtained, by the action of bromine water upon the dibromopyromucic acid melting at 186°, a substance to which he assigned the formula  $C_4H_2Br_2O_2$ , and which he named dibromfumaric aldehyde. He published, however, in the preliminary paper to which we have already alluded,\* no analysis of the substance. We have found that the action of aqueous bromine varies greatly, according to the conditions of the reaction; and although we have been able to prepare a substance whose properties nearly correspond to Toennies's description of the dibromfumaric aldehyde, we have not succeeded in making the yield satisfactory. If one molecule of bromine is slowly added by means of a current of air to the acid suspended in water, the color of the bromine gradually disappears, a part of the acid remains unaltered, while a part of it is converted into tetrabromfurfuran. After the solution had become colorless, we collected upon a filter the insoluble product, and washed it with a dilute solution of sodic carbonate. On acidifying the alkaline solution, the unaltered acid melting at 191° was precipitated. The solid insoluble in the solution of sodic carbonate dissolved readily in alcohol, and on cooling crystallized in long needles which melted at 64–65°, and gave on analysis the percentage of bromine required by tetrabromfurfuran.

0.2201 grm. substance gave 0.4319 grm. AgBr.

	Calculated for $C_4Br_4O$ .	Found.
Br	83.33	83.52

A portion of the acid had therefore been decomposed according to the equation,



From the aqueous solution which had been filtered from the tetrabromfurfuran and the unaltered acid we obtained by extraction with ether a small quantity of a substance which, when recrystallized from

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\* Berichte d. deutsch. chem. Gesellsch., xii. 1203.

dilute alcohol, melted at  $89^{\circ}$ . This gave on analysis a percentage of bromine which was approximately that required by the formula  $C_4H_2Br_2O_2$ .

0.1884 grm. substance gave 0.2897 grm. AgBr.

	Calculated for $C_4H_2Br_2O_2$ .	Found.
Br	66.12	65.45

The formation of the tetrabromfurfuran could be avoided almost entirely by the rapid addition of the bromine. Still, rather more than one molecule of bromine was necessary for complete oxidation of the acid, and the purification of the product was difficult. The ethereal extract left on evaporation a viscous residue, which rarely solidified when allowed to stand in vacuo over sulphuric acid. By extracting this viscous residue with boiling water, we succeeded, however, in obtaining a crystalline product which melted at  $90-91^{\circ}$ , but which gave on analysis too low a percentage of bromine (I.). Since it seemed not improbable that the substance contained mucobromic acid, we dissolved it in a dilute solution of sodic carbonate, and extracted it from the alkaline solution with ether; but the percentage of bromine was unaltered (II.). By sublimation in a stream of carbonic dioxide, however, we obtained a product which melted at  $89-90^{\circ}$ , and gave the required percentage of bromine (III.).

- I. 0.1496 grm. substance gave 0.2295 grm. AgBr.
- II. 0.1981 grm. substance gave 0.2955 grm. AgBr.
- III. 0.1340 grm. substance gave 0.2089 grm. AgBr.

	Calculated for $C_4H_2Br_2O_2$ .	I.	Found. II.	III.
Br	66.12	63.57	63.48	66.36

This substance is readily soluble in alcohol, ether, chloroform, or benzol, more sparingly soluble in ligroin. It is readily soluble in hot water, more sparingly in cold, and crystallizes from aqueous solution in small prisms which often form lattice-like aggregations. By oxidation it yields mucobromic acid, and it must therefore be considered to be dibrommaleic aldehyde. The difficulty of its preparation in quantity made it impossible for us to study it more in detail at present, but we hope to return to it at some future time.

*Action of Nitric Acid.*

Dilute nitric acid oxidizes the  $\beta\gamma$ -dibrompyromucic acid readily on heating. Carbonic dioxide is given off, and the solution then contains mucobromic and dibrommaleic acids. Toennies's erroneous statement that his acid was with difficulty oxidized even by strong nitric acid was doubtless due to the fact that but little hydrobromic acid is formed by the oxidation. For the complete oxidation of the acid we have found two parts of strong nitric acid (sp. gr. 1.42) diluted with five times its weight of water sufficient. After the reaction was over, we extracted with ether and treated the white crystalline residue left on evaporation of the ether with small quantities of cold water. The sparingly soluble mucobromic acid was thus left undissolved, and its identity proved by its melting-point ( $120-121^\circ$ ) and by analysis.

0.2040 grm. substance gave 0.2967 grm. AgBr.

	Calculated for $C_4H_2Br_2O_3$ .	Found.
Br	62.02	61.90

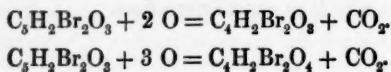
The strongly acid aqueous solution was evaporated to dryness and the residue again treated with a small amount of cold water, in order to insure the removal of the mucobromic acid. The solution thus obtained was neutralized with baric carbonate, the barium salt precipitated with alcohol and recrystallized from water. The air-dried salt then proved to contain a percentage of barium, agreeing with that required by baric dibrommaleate.

0.5138 grm. of the air-dried salt gave on ignition with  $H_2SO_4$  0.2691 grm.  $BaSO_4$ .

	Calculated for $BaC_4Br_2O_4 \cdot 2 H_2O$ .	Found.
Ba	30.78	30.80

The acid obtained from this barium salt was converted into its anhydride by sublimation, and its identity with dibrommaleic anhydride was shown by its melting-point,  $114-115^\circ$ .

The oxidation of  $\beta\gamma$ -dibrompyromucic acid with dilute nitric acid may therefore be expressed by the equations,



## TRIBROMPYROMUCIC ACID.

Tribrompyromucic acid can readily be made from  $\delta$ -monobrompyromucic tetrabromide by the action of an alcoholic solution of sodic hydrate. Although, as has already been remarked, this acid is formed through secondary reactions in the preparation of the dibrompyromucic acids from pyromucic tetrabromide, we have obtained in this way but a small quantity of the acid, and have prepared most of the material we have needed for the investigation from monobrompyromucic acid. The formation of the tribrompyromucic acid by the action of bromine upon the  $\beta\gamma$ -dibrompyromucic acid has already been noticed. Since the hydrogen of the isomeric dibrompyromucic acid cannot be directly replaced by bromine, tribrompyromucic acid cannot be made by the direct action of bromine upon pyromucic acid.

In the decomposition of the monobrompyromucic tetrabromide we have found a low temperature and a concentrated solution of sodic hydrate advantageous. The sodium salt of the tribrompyromucic acid is but sparingly soluble in alcohol, and may be separated by filtration. The alcoholic mother-liquors proved to contain a substance insoluble in water and readily volatile with the vapor of alcohol. For its isolation we precipitated the excess of sodic hydrate with carbonic dioxide, distilled the filtered solution, and precipitated the distillate by the addition of water. The heavy oil which was thus thrown down we dried with calcic chloride, and submitted it to fractional distillation in an atmosphere of carbonic dioxide under diminished pressure. After several distillations, by far the greater portion of the oil showed the constant boiling-point  $96-98^\circ$  under a pressure of 20 mm., and we were unable to isolate other definite products. An analysis showed the main product to be a tribromfurfuran.

0.3417 grm. substance gave 0.6299 AgBr.

	Calculated for $C_4HBr_3O$ .	Found.
Br	78.68	78.39

Tribromfurfuran had, therefore, been formed from the monobrompyromucic tetrabromide according to the equation,



The sodium salt which had separated from the alcoholic solution we acidified with hydrochloric acid, and recrystallized the acid thus obtained from dilute alcohol, and finally from water.

- I. 0.6837 grm. substance gave 0.4266 grm.  $\text{CO}_2$  and 0.0221 grm.  $\text{H}_2\text{O}$ .  
 II. 0.1658 grm. substance gave 0.2684 grm.  $\text{AgBr}$ .  
 III. 0.1885 grm. substance gave 0.3047 grm.  $\text{AgBr}$ .

	Calculated for $\text{C}_5\text{HBr}_3\text{O}_3$	I.	Found. II.	III.
C	17.20	17.02		
H	0.28	0.36		
Br	68.77		68.90	68.79

Tribrompyromucic acid crystallizes in minute clustered needles which melt at  $218-219^\circ$ . It is readily soluble in alcohol or ether, somewhat sparingly soluble in chloroform or benzol, and very sparingly soluble in carbonic disulphide or ligroin. It dissolves with difficulty even in boiling water, and the hot solution deposits the greater part of the acid on cooling. In order to determine the solubility of the acid in cold water, we boiled the saturated solution with baric carbonate and precipitated with sulphuric acid the barium dissolved.

- I. 43.8259 grm. of a solution saturated at  $19^\circ$  gave 0.0105 grm.  $\text{BaSO}_4$ .  
 II. 42.6017 grm. of a solution saturated at  $19^\circ$  gave 0.0101 grm.  $\text{BaSO}_4$ .

According to these determinations the aqueous solution saturated at  $19^\circ$  contained the following percentages of the acid:—

I.	II.
0.072	0.071

*Baric Tribrompyromucate*,  $\text{Ba}(\text{C}_5\text{Br}_3\text{O}_3)_2 \cdot 3 \text{H}_2\text{O}$ .—The barium salt we prepared by precipitating a solution of baric chloride with a solution of the acid in dilute ammoniac hydrate and recrystallizing from boiling water the salt thus obtained. It crystallized in dendritic needles, which, when air-dried, contained three molecules of water, nearly all of which it lost over sulphuric acid.

- I. 1.1629 grm. of the salt lost at  $120^\circ$  0.0695 grm.  $\text{H}_2\text{O}$ .  
 II. 1.6160 grm. of the salt lost at  $120^\circ$  0.0970 grm.  $\text{H}_2\text{O}$ .

	Calculated for $\text{Ba}(\text{C}_5\text{Br}_3\text{O}_3)_2 \cdot 3 \text{H}_2\text{O}$	I.	Found. II.
$\text{H}_2\text{O}$	6.09	5.98	6.00

- I. 0.6867 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1878 grm.  $\text{BaSO}_4$ .

- II. 0.8009 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.2192 grm.  $\text{BaSO}_4$ .

	Calculated for $\text{Ba}(\text{C}_5\text{Br}_3\text{O}_3)_2$ .	Found.	
		I.	II.
Ba	16.44	16.08	16.07

The solubility of the salt in cold water we determined by precipitating the saturated solution with sulphuric acid.

- I. 36.2176 grm. of a solution saturated at  $20^\circ$  gave 0.0197 grm.  $\text{BaSO}_4$ .  
 II. 32.6167 grm. of a solution saturated at  $20^\circ$  gave 0.0181 grm.  $\text{BaSO}_4$ .

The aqueous solution saturated at  $20^\circ$ , therefore, contained the following percentages of the anhydrous salt:—

I.	II.
0.19	0.20

*Calcic Tribromopyromucate*,  $\text{Ca}(\text{C}_5\text{Br}_3\text{O}_3)_2 \cdot 4\text{H}_2\text{O}$ . — The calcium salt we prepared by precipitating an ammoniacal solution of the acid with calcic chloride. When recrystallized from hot water, it formed clusters of fine dendritic needles, which were permanent in the air, but effloresced over sulphuric acid.

- I. 1.5509 grm. of the salt lost at  $120^\circ$  0.1385 grm.  $\text{H}_2\text{O}$ .  
 II. 0.9115 grm. of the salt lost at  $120^\circ$  0.0799 grm.  $\text{H}_2\text{O}$ .

	Calculated for $\text{Ca}(\text{C}_5\text{Br}_3\text{O}_3)_2 \cdot 4\text{H}_2\text{O}$ .	Found.	
		I.	II.
$\text{H}_2\text{O}$	8.91	8.93	8.77

- I. 0.5885 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1060 grm.  $\text{CaSO}_4$ .  
 II. 0.6364 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1122 grm.  $\text{CaSO}_4$ .

	Calculated for $\text{Ca}(\text{C}_5\text{Br}_3\text{O}_3)_2$ .	Found.	
		I.	II.
Ca	5.44	5.30	5.18

In order to determine the solubility of the salt in cold water, we precipitated the saturated solution with ammonic oxalate, and converted the calcic oxalate thus obtained into calcic sulphate by ignition with sulphuric acid.

- I. 34.5554 grm. of a solution saturated at  $20^{\circ}$  gave 0.0346 grm.  $\text{CaSO}_4$ .  
 II. 27.6386 grm. of a solution saturated at  $20^{\circ}$  gave 0.0267 grm.  $\text{CaSO}_4$ .

The aqueous solution saturated at  $20^{\circ}$ , therefore, contained the following percentages of the anhydrous salt:—

I.	II.
0.54	0.57

*Argentio Tribrompyromucate*,  $\text{AgC}_5\text{Br}_3\text{O}_3$ . — Argentio nitrate gives even in the cold aqueous solution of the acid a crystalline precipitate of the silver salt, which is sparingly soluble even in boiling water. It may readily be prepared by precipitating a soluble salt of the acid with argentio nitrate and washing with hot water.

0.2977 grm. of the salt gave 0.1242 grm.  $\text{AgBr}$ .

	Calculated for $\text{AgC}_5\text{Br}_3\text{O}_3$ .	Found.
Ag	23.68	23.96

*Sodio Tribrompyromucate*,  $\text{NaC}_5\text{Br}_3\text{O}_3 \cdot \text{H}_2\text{O}$ . — The sodium salt we prepared by dissolving the acid in a dilute solution of sodio carbonate. The salt was not very soluble in cold water, and crystallized, on cooling the aqueous solution, in fine woolly needles, which contained one molecule of water and slowly effloresced over sulphuric acid.

- I. 1.0434 grm. of the air-dried salt lost at  $108^{\circ}$  0.0457 grm.  $\text{H}_2\text{O}$ .  
 II. 1.1171 grm. of the air-dried salt lost at  $112^{\circ}$  0.0531 grm.  $\text{H}_2\text{O}$ .

	Calculated for $\text{NaC}_5\text{Br}_3\text{O}_3 \cdot \text{H}_2\text{O}$ .	Found.	
		I.	II.
$\text{H}_2\text{O}$	4.63	4.38	4.76

- I. 0.5947 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1132 grm.  $\text{Na}_2\text{SO}_4$ .  
 II. 0.5036 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.0987 grm.  $\text{Na}_2\text{SO}_4$ .

	Calculated for $\text{NaC}_5\text{Br}_3\text{O}_3$ .	Found.	
		I.	II.
Na	6.20	6.17	6.35

*Potassic Tribrompyromucate*,  $\text{KC}_5\text{Br}_3\text{O}_3 \cdot \text{H}_2\text{O}$ . — The potassium salt we prepared by neutralizing a dilute solution of potassic carbonate with the acid. It was not very soluble in cold water, and crystallized,

on cooling the aqueous solution, in globular aggregations of fine needles. The air-dried salt contained one molecule of water and slowly effloresced over sulphuric acid.

I. 1.6850 grm. of the air-dried salt lost at  $120^{\circ}$  0.0753 grm.  $\text{H}_2\text{O}$ .

II. 1.7346 grm. of the air-dried salt lost at  $112^{\circ}$  0.0784 grm.  $\text{H}_2\text{O}$ .

	Calculated for $\text{KC}_5\text{Br}_3\text{O}_8 \cdot \text{H}_2\text{O}$ .	Found.	
		I.	II.
$\text{H}_2\text{O}$	4.44	4.47	4.52

I. 0.6838 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1522 grm.  $\text{K}_2\text{SO}_4$ .

II. 0.5826 grm. of the anhydrous salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.1319 grm.  $\text{K}_2\text{SO}_4$ .

	Calculated for $\text{KC}_5\text{Br}_3\text{O}_8$ .	Found.	
		I.	II.
K	10.10	10.09	10.16

*Ethyl Tribrompyromucate*,  $(\text{C}_2\text{H}_5)_3\text{C}_5\text{Br}_3\text{O}_8$ .—The ethyl ether we have prepared by warming the silver salt of the acid with ethyl iodide, and also by heating an alcoholic solution of the acid with concentrated sulphuric acid. In the latter case we found it convenient to use two parts of absolute alcohol and one part of concentrated sulphuric acid to one part of the acid. After heating for several hours at  $100^{\circ}$ , we precipitated the ether by the addition of water, washed it with a dilute solution of sodic carbonate, and recrystallized it from alcohol. It formed clear rectangular prisms, which melted at  $104^{\circ}$ , and have little or no odor at ordinary temperatures. It is readily soluble in ether, chloroform, benzol, or carbonic disulphide, somewhat more sparingly soluble in ligroin. It is quite sparingly soluble even in boiling alcohol. The material used in Analysis II. was made from the silver salt.

I. 0.1785 grm. substance gave 0.2677 grm. AgBr.

II. 0.1526 grm. substance gave 0.2284 grm. AgBr.

	Calculated for $(\text{C}_2\text{H}_5)_3\text{C}_5\text{Br}_3\text{O}_8$ .	Found.	
		I.	II.
Br	63.66	63.83	63.71

*Tribrompyromucamide*,  $\text{C}_5\text{Br}_3\text{O}_2\text{NH}_2$ .—Although ethyl tribrompyromucate is but slowly attacked by concentrated aqueous ammonia at ordinary temperatures, it is readily decomposed at  $100^{\circ}$  in sealed tube with the formation of tribrompyromucamide. The resulting product was purified by recrystallization from alcohol, and formed then fine

needles which melted at 222–223°. It was readily soluble in hot alcohol, quite sparingly soluble in ether, chloroform, or benzol, insoluble in carbonic disulphide or ligroin. It was nearly insoluble even in boiling water.

0.6792 grm. substance gave 23.5 c.c. of moist nitrogen at 22° and under a pressure of 744 mm.

	Calculated for $C_5Br_3O_3NH_2$ .	Found.
N	4.02	3.92

*Action of Bromine and Water.*

Bromine acts but slowly upon tribrompyromucic acid suspended in water, and even if the acid be finely subdivided a portion of it escapes decomposition. Since little action was visible when the vapor of bromine was slowly led in by means of a current of air, we added exactly one molecule of bromine, and then collected upon a filter the insoluble matter which remained. A portion of this dissolved in a dilute solution of sodic carbonate, and could be reprecipitated by the addition of hydrochloric acid. The properties of the precipitated acid and its melting-point (216°) showed it to be unaltered tribrompyromucic acid. The portion which was insoluble in the alkaline solution was dissolved in boiling alcohol, and on cooling crystallized in long slender needles which melted at 63–64°. An analysis gave the percentage of bromine required by tetrabromfurfuran.

0.2217 grm. substance gave 0.4359 grm. AgBr.

	Calculated for $C_4Br_4O$ .	Found.
Br	83.33	83.68

The aqueous solution filtered from the tetrabromfurfuran and the unaltered tribrompyromucic acid yielded, on extraction with ether, dibrommaleic acid in quantity too small to admit of analysis, although its identity could readily be established by the melting-point of its anhydride (114–115°). With aqueous bromine, therefore, tribrompyromucic acid yields essentially tetrabromfurfuran and carbonic dioxide according to the equation,



*Action of Nitric Acid.*

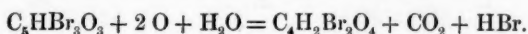
Tribrompyromucic acid is much less readily attacked by dilute nitric acid than either of the dibrompyromucic acids, and to effect its oxida-

tion we were obliged to use three parts of strong nitric acid (sp. gr. 1.42) diluted with twice its weight of water to one part of the acid. After continued boiling the acid was dissolved, and from the clear solution, by extraction with ether, we were able to isolate only dibrommaleic acid, which melted at  $125^{\circ}$ , and gave by sublimation an anhydride which melted at  $114-115^{\circ}$ . The barium salt was prepared by neutralizing the acid in aqueous solution with baric carbonate, and precipitating the filtered solution with alcohol. This salt, when recrystallized from water and dried by exposure to the air, gave the percentage of barium required by baric dibrommaleate.

0.5259 grm. of the air-dried salt gave on ignition with  $\text{H}_2\text{SO}_4$  0.2765 grm.  $\text{BaSO}_4$ .

	Calculated for $\text{BaC}_4\text{Br}_2\text{O}_4 \cdot 2 \text{H}_2\text{O}$ .	Found.
Ba	30.78	30.91

By the oxidation of tribrompyromucic acid with nitric acid dibrommaleic acid is, therefore, formed according to the equation,



#### THEORETICAL CONSIDERATIONS.

It is evident that definite conclusions as to the relative position of the bromine atoms in the various substituted pyromucic acids which we have described may be drawn from the products which result from the oxidation, and at the same time it seems to us that certain of our observations enable us to discriminate between the two structure formulæ for pyromucic acid which have hitherto seemed most probable. The behavior of pyromucic acid with phosphorus pentachloride, as shown by the experiments of Liës-Bodart,\* or of its ethyl ether with acetyl chloride, as shown by Schmelz and Beilstein,† rendered it certain that pyromucic acid could not contain its third oxygen atom in the form of hydroxyl. Limpricht's‡ experiments with furfuran (tetraphenol), and the indifference shown by pyromucic acid toward nascent hydrogen, excluded the possibility of the presence of an aldehyde or ketone group. The absence of both of these forms of oxygen has more recently been confirmed by the experiments of Odernheimer,§

\* Ann. Chem. u. Pharm., c. 327.

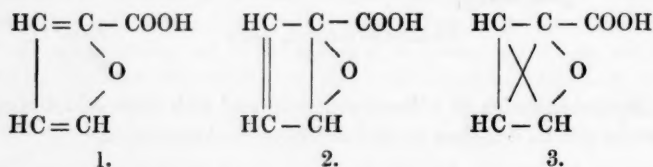
† Ibid., Suppl., iii. 276.

§ Ber. der deutsch. chem. Gesell., xvi. 2988.

‡ Ibid., clxv. 282.

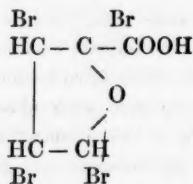
who showed that pyromucic acid was not attacked by hydroxylamine, and of Wagner,\* who failed to reduce the furfuran oxygen with zinc ethyl. Of the known forms in which oxygen occurs, therefore, there remains only the oxide form, C-O-C, which can be assumed to exist in the molecule of pyromucic acid. Moreover, Baeyer † has shown by the conversion of furfurol into furfuracrylic, furfurpropionic, furonic, and pimelic acids that the carboxyl group of the pyromucic acid is attached directly to one of these two carbon atoms which bear the oxygen atom.

In accordance with these facts, Baeyer has proposed the following three formulæ for pyromucic acid, the first of which he suggested in 1870,‡ the other two in 1877 §:—



Of these three formulæ, however, Baeyer preferred the second, since it appeared to explain most readily the formation from pyromucic acid of derivatives of fumaric acid which Limpricht had observed.

Since pyromucic acid forms an addition product containing four atoms of bromine, to this tetrabromide must be assigned in any case one and the same formula.



The simultaneous formation from this tetrabromide of two dibromopyromucic acids, which we have observed, one of which can be converted by oxidation into monobromofumaric (or monobromomaleic) acid, the second into dibromomaleic (or mucobromic) acid, seems to us to necessitate the rejection of the second formula. From the pyromucic

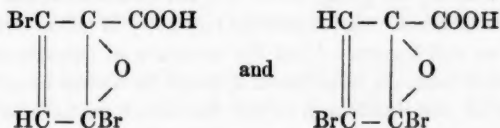
\* Ber. der deutsch. chem. Gesell., xvii. 1967.

† Ibid., x. 1358.

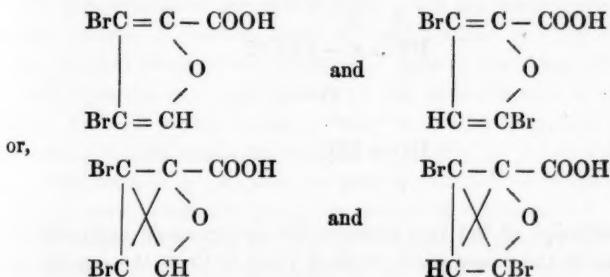
‡ Ibid., iii. 517.

§ Ibid., x. 1361.

tetrabromide whose formula is given above two isomeric dibromopyromucic acids can in any case be formed; but if the second formula for pyromucic acid be adopted, these would necessarily have the structure,



both of which would yield on oxidation monobromofumaric or monobromomaleic acid. On the other hand, the adoption of either the first or the third formula for pyromucic acid would give for the resulting dibromopyromucic acids the forms,

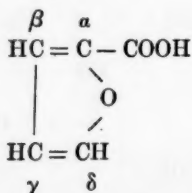


In either case, the oxidation products which we have observed would find in these formulæ a natural explanation.

While either of these two formulæ will explain the facts which we have observed, it seems to us that there can be no doubt that preference should be given to the first. Aside from the difficulty of explaining by means of the third formula the formation of the pyromucic tetrabromide, and the re-establishment of the carbon ties by the action of caustic alkalies, the formation of Heintzlemann's dehydromucic acid from mucic acid, which certainly is a dicarboxyfurfuran, would necessitate the assumption of a mode of dehydration in whose support, so far as we are aware, no analogous cases can be advanced. On the other hand, the ready formation of the lactones, as shown by the brilliant researches of Fittig, renders the formation of a stable oxide by the elimination of water involving hydroxyl groups attached to the first and fourth carbon atoms a matter in every way probable. We cannot deny that the adoption of the first formula renders the

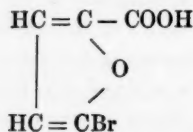
explanation of the formation of derivatives of fumaric or maleic acid by oxidation somewhat difficult (the same objection applies, of course, to a still greater degree to the third formula); and still we cannot consider this objection a serious one, while the normal behavior of substances containing the group C-C-C-C is not established, and the ease with which molecular rearrangements take place in non-saturated compounds is so well known. Until the structure of fumaric and maleic acids is more definitely established, it would be useless to attempt any discussion of the significance of the fact which we have established, that maleic acid and its derivatives, and not the corresponding derivatives of fumaric acid, are the first products formed in the decomposition of the substituted pyromucic acids.

If the carbon atoms in pyromucic acid are designated as usual, beginning with the carboxyl group,

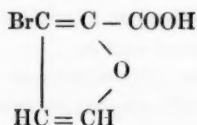


the constitution of the two isomeric dibromopyromucic acids may be expressed by the names which we have given to them, the  $\beta\gamma$ -dibromopyromucic acid (melting-point  $191-192^\circ$ ), passing by oxidation into dibrommaleic acid, while the  $\beta\delta$ -dibromopyromucic acid yields monobrommaleic acid.

The determination of the constitution of the monobrompyromucic acids is a matter of no difficulty. The oxidation of the monobrompyromucic acid melting at  $183-184^\circ$  directly to maleic or fumaric acid shows that its bromine must be in the  $\delta$ -position, and its formula,

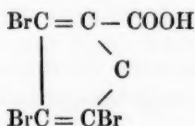


On the other hand, the monobrompyromucic acid melting at  $128-129^\circ$ , since it is formed by the reduction of either of the two dibrompyromucic acids, must have its bromine atom at  $\beta$ , and its formula is therefore



By oxidation with nitric acid it gives, as it should, monobromfumaric acid.

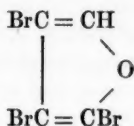
Since all the furfuran hydrogens are replaced by bromine in tribrompyromucic acid, but one form of the acid is possible, and that is



Of the substituted pyromucic acids which we have studied, those which contain a bromine atom in the  $\delta$ -position give, by oxidation with bromine water, dibasic acids, while those in which the  $\delta$ -hydrogen is not thus replaced yield ultimately the aldehyde acid, mucobromic acid. Although we are unable to follow at present the successive steps by which this oxidation proceeds, it may fairly be inferred that the  $\alpha$ -carbon atom is in any case completely oxidized, while the  $\delta$ -carbon atom appears in the aldehyde group whenever this is formed.

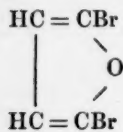
The strong analogies between the derivatives of furfuran and of benzol have frequently been pointed out during the past few years. It is interesting to note that by the action of bromine upon pyromucic acid the  $\delta$  and  $\beta$  hydrogen atoms are successively replaced. If the group  $\text{CH}=\text{CH}$  be substituted for the oxygen of furfuran, these become respectively the para and ortho positions of the aromatic series. While benzoic acid itself is converted into metabrombenzoic acid by the action of bromine, the formation of para and ortho derivatives under these conditions is more frequently observed in the aromatic series.

While we, unfortunately, have been able as yet to obtain no direct evidence as to the constitution of the substituted furfurans which we have described, there can be little doubt as to their structure. The tribromfurfuran obtained in the preparation of tribrompyromucic acid must certainly have the formula

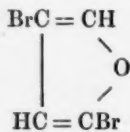


and the tribromfurfuran obtained from the crude pyromucic tetrabromide is undoubtedly identical with it.

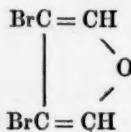
Of the four formulæ for dibromfurfuran, which are possible if the formulæ of furfuran we have adopted be correct,



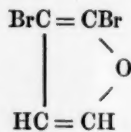
1.



2.



3.



4.

the first undoubtedly represents the structure of a dibromfurfuran which has already been described in a preliminary paper by Mr. George T. Hartshorn and one of us.\* The mode of its formation, and its reactions, leave no possible doubt as to its constitution. It seems to us that there can be no reasonable doubt that the two dibromfurfurans which we have just described must have the structure represented by the second and third formulæ, corresponding to the formulæ of the two dibrompyromucic acids formed at the same time. The latter formula, then, probably represents the more stable substance of lower boiling-point.

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\* Ber. der deutsch. chem. Gesell., xviii. 448

## VI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.ON THE ACTION OF CHROMIC SUPERFLUORIDE ON  
BENZOIC ACID.

BY C. LORING JACKSON AND GEORGE T. HARTSHORN.

Communicated May 13, 1885.

As the chromic superfluoride is instantly decomposed by water with the formation of chromic anhydride and hydrofluoric acid, we undertook the experiments described in the following paper in the hope that organic compounds containing hydroxyl would act in a similar way; and since Mallet's\* determination of the vapor-density of hydrofluoric acid obliges us to assign it the formula  $H_2F_2$ , that thus we might obtain organic substances, in which the oxygen of the hydroxyl was replaced by two atoms of fluorine, as in fluosilicic acid. This hope has not been realized in the case of benzoic acid, with which we began our experiments, as the chromic superfluoride left the hydroxyl entirely unaltered; but, on the other hand, it has led us to a very interesting result, as the products of the reaction were chromic fluoride ( $Cr_2F_6$ ) and a difluorbenzoic acid, and therefore we have achieved for the first time, so far as we can find, the direct substitution of the hydrogen in an organic substance by fluorine. Preliminary experiments with acetic acid and benzol seem to show that the reaction is a general one,—in both cases the chromic superfluoride was reduced to a lower fluoride of chromium,—and there is good promise, therefore, that it will prove of service in adding new members to the class of fluorine organic compounds, as yet so meagrely represented.

We have not made a complete study of the difluorbenzoic acid, but have contented ourselves with doing enough to characterize it thoroughly, as we are anxious to avoid any interference with Paterno, who has already begun the investigation of organic bodies in which

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\* Am. Chem. J., iii. 189.

hydrogen is replaced by fluorine. Nor do we intend to continue our experiments on acetic acid and benzol, as Paterno has announced that he is at work on the fluorine derivatives of both these substances. We wish, however, to reserve for our future study the action of chromic superfluoride on all other organic substances.

The remainder of the paper consists of the detailed account of our experimental work.

### *Action of Chromic Superfluoride on Benzoic Acid.*

The chromic superfluoride was made by the action of 180 gr. of fuming sulphuric acid on 60 gr. of potassic dichromate and 100 gr. of calcic fluoride, both of which must be perfectly dry. If the fuming sulphuric acid is very strong, it should be diluted with ordinary strong sulphuric acid, as, if this precaution is neglected, the action is so violent that it cannot be controlled, a large amount of the superfluoride is wasted, and in extreme cases the cover may be blown off the lead retort. The lead retort used was of the cylindrical form figured in most text-books for making the aqueous solution of hydrofluoric acid; the fuming sulphuric acid was first introduced, the fluor-spar and potassic dichromate previously thoroughly mixed were then added, and stirred in with an iron rod, the cover put on, and the reaction started by a gentle heat. As soon as faint white fumes appear at the exit tube, the lamp should be removed, and, after the first violent evolution of gas has slackened, the action can be made to proceed smoothly by a gentle heat, although it is hard to avoid occasional rushes of gas. It is hardly necessary to say that the work should be carried on under a good hood, and the hands protected by india-rubber gloves. After the process is finished, the retort should be emptied before it has become cold, as after the residue has hardened its removal is both difficult and tedious.

The chromic superfluoride obtained in this way is not free from hydrofluoric acid, to judge from the white fumes which were observed mixed with the dark red heavy vapor; but it was pure enough for our purpose, and was allowed to act directly on the solid benzoic acid, which was spread in a layer rather less than a centimeter thick over the bottom of a platinum dish, or on its cover; for this purpose the lead pipe, which formed the exit tube of the retort, was brought down so that it nearly touched the surface of the acid. Absolute contact must be avoided, as in this case the tube soon becomes stopped up with the fused product. With a rapid stream of the superfluoride the action

is vigorous, the benzoic acid fusing and forming a black crust, which was made to spread over the whole surface by moving the dish when necessary; the crust was then removed,\* and the same action repeated with fresh benzoic acid, until all the superfluoride was exhausted. In this way 180 gr. of the crusts could be obtained in a single operation. If the stream of superfluoride was not rapid, the benzoic acid was apt to become covered with chromic anhydride, probably from a trace of moisture in the acid, and this not infrequently gave rise to unimportant deflagrations; but the amount of chromic anhydride formed even by this secondary reaction is very small, almost the whole of the chromic superfluoride being converted directly into the green chromic fluoride  $\text{Cr}_2\text{F}_6$ .

To obtain the difluorbenzoic acid from the crude product it was dissolved in a strong solution of sodic carbonate, and, after the chromic hydrate had been removed by filtration, fractionally precipitated with hydrochloric acid, the liquid being boiled with the separated benzoic acid after each precipitation. We found it wisest to divide the whole into two about equal fractions at first, and then to fraction the least acid portion again, when all the difluorbenzoic acid collected in the least acid fraction, which should be made very small; this was then boiled with water, and the residue purified by recrystallization from boiling benzol and sublimation. The yield of difluorbenzoic acid is only 1.5 per cent of the benzoic acid used.

Having obtained the difluorbenzoic acid, we next tried to detect the presence of monofluorbenzoic acid, and for this purpose examined the acid contained in the hot aqueous filtrate from boiling the difluor acid with water, and also the fraction immediately preceding the least acid one. As the metafluorbenzoic acid melts at  $123^\circ$ – $124^\circ$  according to Paterno and Oliveri,† the melting-point was of no assistance to us, and we have accordingly made a number of analyses of the barium salts of these fractions, both before and after a repetition of the fractional saturation, which have given results varying from 35.81 to 35.99 per cent of barium; baric benzoate contains 36.15 per cent, baric fluorbenzoate 33.01 per cent.‡ We also thought it might be contained in a mixture of acids, obtained by boiling the crude product with insufficient water, melting sometimes as low as  $102^\circ$ ; but this on fractional neutralization

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\* We think it right to mention that both of us were poisoned, one severely, by the crude product, which was spilt on our clothes in removing the crusts from the platinum dishes.

† Ber. d. ch. G., 1882, p. 1197.

‡ The most acid fractions were also pure benzoic acid, as was to be expected.

was divided into difluorbenzoic acid and benzoic acid, as proved by analyses of the barium salt. We are convinced, therefore, that no monofluorbenzoic acid is formed by the action of chromic superfluoride on benzoic acid, but the products of the reaction are only difluorbenzoic acid and chromic fluoride with a little chromic anhydride as an impurity.

*Difluorbenzoic Acid,  $C_6H_4F_2COOH$ .*

The acid prepared and purified, as described above, appears when sublimed in white flattened needles looking very much like benzoic acid, when crystallized from alcohol or benzol in short fine needles; it sublimes at a temperature far below its melting-point,  $232^\circ$  (uncor.), but with much more difficulty than benzoic acid, and burns with a strongly green-bordered flame. It is essentially insoluble in cold water, and only slightly soluble in hot, the boiling solution depositing a few crystalline flocks of the acid on cooling; not very freely soluble in cold alcohol or benzol, but freely in either of these solvents when hot, very soluble in ether or glacial acetic acid, less so in methyl alcohol, and almost insoluble in ligroine, or carbonic disulphide. Benzol is the best solvent for purifying it by crystallization.

Its composition was established by the following combustions:—

- I. 0.2549 gr. of substance burnt with plumbic chromate in a closed tube\* gave 0.4964 gr. of carbonic dioxide and 0.0982 gr. of water.
- II. 0.1595 gr. gave 0.3131 gr. of carbonic dioxide and 0.0506 gr. of water.

	Calculated for $C_7H_4F_2O_2$ .	I.	Found. II.
Carbon	53.16	53.13	53.52
Hydrogen	2.53	4.28	3.53

The ammoniac difluorbenzoate is decomposed by evaporating its solution to dryness; but a solution freed from ammonia by boiling gave white precipitates with plumbic acetate, and mercurous, mercuric, and argentic nitrates, and a bluish white precipitate with cupric sulphate.

*Baric Difluorbenzoate,  $Ba(C_6H_4F_2O_2)_2$ ,* made by boiling the acid with baric carbonate and water, crystallizes in white scales, and contains no water of crystallization even when only air-dried.

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\* We found it impossible to obtain agreeing results when the combustion was performed in the ordinary way with oxygen.

- I. 0.2716 gr. of the salt dried at  $110^{\circ}$  gave 0.1395 gr. of baric sulphate.  
 II. 0.2674 gr. gave 0.1378 gr. of baric sulphate.

	Calculated for $\text{Ba}(\text{C}_7\text{H}_3\text{F}_2\text{O}_2)_2$	I.	Found.	II.
Barium	30.38	30.20		30.28

Its solubility in water was determined according to the method of Victor Meyer:—

- I. 1.5814 gr. of a solution saturated at  $15^{\circ}$  gave 0.0188 gr. of the salt by evaporation.  
 II. 2.6260 gr. gave 0.0310 gr. of the salt.

Therefore, the solution saturated at  $15^{\circ}$  contains the following percentages of the salt:—

I.	II.
1.19	1.18

*Calcic Difluorbenzoate*,  $\text{Ca}(\text{C}_7\text{H}_3\text{F}_2\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$ .

This very characteristic salt, made by boiling the acid with calcic carbonate and water, begins to crystallize out, as soon as the liquid is somewhat concentrated, in bundles of silky needles, frequently a centimeter long, and slightly branched at a very acute angle.

- I. 0.7886 gr. of the air-dried salt lost 0.1058 gr. at  $100^{\circ}$ .  
 II. 0.3605 gr. lost 0.0495 gr.

	Calculated for $\text{Ca}(\text{C}_7\text{H}_3\text{F}_2\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$	I.	Found.	II.
Water	13.28	13.42		13.73

- I. 0.2440 gr. of the salt dried at  $100^{\circ}$  gave 0.0914 gr. of calcic sulphate.  
 II. 0.3024 gr. gave 0.1153 gr. of calcic sulphate.

	Calculated for $\text{Ca}(\text{C}_7\text{H}_3\text{F}_2\text{O}_2)_2$	I.	Found.	II.
Calcium	11.30	11.02		11.21

Its solubility in water was determined according to the method of Victor Meyer:—

- I. 2.0134 gr. of a solution saturated at  $15^{\circ}$  gave 0.0100 gr. of the anhydrous salt by evaporation.  
 II. 5.1731 gr. gave 0.0256 gr. of the anhydrous salt.

Therefore, the solution saturated at 15° contains the following percentages of the anhydrous salt.

I.	II
0.50	0.49

The calcium salt when heated with an excess of lime gives off a combustible vapor, probably difluorbenzol, as only 4 per cent of fluorine was removed from the acid in this way, but we do not intend to try to isolate this product for fear of interfering with Paterno. This observation was made in an attempt to determine the fluorine in the acid by Piria's method,\* which showed that a much larger layer of alkali than could be obtained in this way was needed to remove the fluorine from the organic compound. We propose in our subsequent work to make another effort to solve this difficult problem in organic analysis.

It is to be observed that the large percentages of hydrogen obtained in the combustion of the acid correspond to the formula  $C_6H_5F_2CO_2H$  better than to  $C_6H_3F_2CO_2H$ , and that our other analytical work is not capable of deciding between these formulas. The formula  $C_6H_5F_2CO_2H$  would be that of an oxybenzoic acid containing two atoms of fluorine instead of one of oxygen ( $\begin{smallmatrix} C_6H_4COOH \\ F_2H \end{smallmatrix}$ ), and although the difficulty of removing the fluorine from the acid rendered this formula highly improbable, we have thought it necessary to prove that it was incorrect. For this purpose we treated the acid with a large excess of potassic hydrate in alcoholic solution, and analyzed the potassium salt, which can be precipitated by ether in broad silvery scales, when we obtained an amount of potassium corresponding to the formula  $C_6H_3F_2CO_2K$ .

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\* H. Schiff, Ann. Chem., cxcv. 293.

## VII.

ON THE INFLUENCE OF MAGNETIC STRESS UPON  
THE CAPACITY OF AN ELECTRIC CONDENSER.

BY A. S. KIMBALL.

Communicated June 10, 1885.

RECENT work in the laboratory of the Worcester Institute of Industrial Science has apparently established results of which the following is a brief statement.

When an electric condenser placed between the poles of a powerful electro-magnet is charged and discharged through a galvanometer, its capacity as indicated by the swing of the needle is increased by the excitement of the magnet, if its lines of force are perpendicular to the plates of the condenser; but if the condenser plates are parallel to these lines, the capacity is diminished. The percentages of increase in one case and decrease in the other are equal in magnetic fields of the same intensity, and these variations from the normal capacity are greater as the intensity of the field increases.

The experiments which led to these conclusions were suggested by Maxwell's statements, which indicate a similarity of stress existing in the electro-static and electro-magnetic fields. Maxwell also says that in a field on which electro-static as well as electro-magnetic action is taking place, we must suppose the one stress superposed on the other.

Several methods of experiment were successively tried, and rejected on account of possible sources of error, before the final disposition of apparatus was reached.

The first trial was with a  $\frac{1}{2}$  microfarad condenser placed on edge between the poles of an electro-magnet. The cores of the magnet were 2 inches in diameter and 13 inches long, and were united by a massive soft iron yoke. Each branch was wound with 275 convolutions of wire through which a current of 11 ampères was driven by a dynamo, about ten feet distant. Movable pole pieces were used, and by varying their distance from each other the intensity of the magnetic field could be increased or diminished at will. The current from the dynamo

measured by a large tangent galvanometer was approximately constant during the whole series of experiments.

This apparatus was placed in a basement about sixty feet from the testing-table on the floor above. A pair of carefully insulated wires made connection between the condenser and the testing-table. On the table was a Thomson reflecting galvanometer of 7,000 ohms resistance, and the charging key. A water battery was used to charge the condensers, and the charging potential varied at need from 3 to 175 volts.

The  $\frac{1}{2}$  microfarad condenser was charged and discharged through a plain key, the magnet being alternately excited and inactive.

Encouraging but not decisive indications were obtained. The variation was so small a part of the total capacity, that it was masked by errors of experiment and observation.

To reduce the deflection of the needle to a manageable amount and yet retain the same variation, if any, a new condenser of about the same capacity was made, and three keys used. By the first, both condensers were charged simultaneously to the same potential; by the second, they were discharged into each other; and by the third, the difference between their charges was discharged through the galvanometer.

The use of three keys was found to introduce great errors, arising from variations in the time given to each of the operations mentioned above, and a new key was made which required but a single motion instead of three. After adopting a uniform time of charging — in the majority of cases fifteen seconds — fairly constant results were obtained, and some of the earlier observations reported are taken from experiments in which this key was used. Ultimately on account of objections to the length of time of charging, as well as to secure greater uniformity in the separate periods allotted to each part of the process, a new key was constructed, which proved very satisfactory in use, and which has been employed exclusively since that time. It consisted of a heavy  $\frac{3}{4}$ -second pendulum furnished with adjustable catches, by whose use it could be made to execute a single vibration through any required amplitude, and could be held suspended at the end of its swing.

The pendulum carried on its under side two insulated metal pieces, from each of which depended three small platinum wires.

These wires in the course of their vibration cut through drops of mercury connected with the poles of the battery, the poles of the condensers, the binding-screws of the galvanometer, and each other, in such a manner as to produce the desired connections.

The amplitude of the vibration was fixed to give about one tenth of a second to the charging, one tenth of a second between the charge and discharge, and one tenth of a second to the discharge into each other, at last leaving the condenser plates in communication through the galvanometer.

The proper insulation of the wires at the key gave some trouble, but was at last secured by imbedding the wires in paraffine at all points of contact with the key, and placing the drops of mercury at the bottom of deep grooves in a paraffine block, separating those in the same groove from each other by a transverse groove of greater depth. In fairly dry weather, this arrangement gave satisfactory results. This key could be used to charge and discharge a single condenser; in fact, in the later experiments it was found better to use but one condenser, regulating its size to make the deflections manageable.

With the apparatus thus arranged and tested for connections and insulation, the labor of experiment was comparatively light. The condensers were charged and discharged several times, the electro-magnet meanwhile being inactive. The dynamo was then set in motion, the magnet excited, and the condensers charged and discharged as before. Usually this process was repeated several times before making any change in the apparatus, as will be seen in the tables which follow. Repeated tests were made to determine whether the dynamo or the electro-magnet by their direct action would affect the scale reading, but no motion of the index line could be detected when the machine was started and stopped by an assistant. This test was repeated, with the battery, condenser, and galvanometer circuits joined, in every combination assumed by them in the course of the experiment.

The magnet circuit was always closed. The charging battery was disconnected from the condensers  $\frac{1}{20}$  of a second before the condensers were put upon the galvanometer.

In these experiments no attempt has been made to obtain accurate quantitative results, and as no care was taken to adjust the galvanometer to the same degree of sensitiveness, the readings in different series of experiments are not comparable.

The directive power of the earth upon the needle was very nearly neutralized by magnets placed near it, so that the torsion of the suspending fibre, which is constantly changing both as to direction and amount, comes to have a larger influence than is desirable upon the results. It is fortunate that the influence of a progressive change of this sort may be largely eliminated by a suitable order of experimentation.

Several tables follow, containing results which seem to warrant the statements with which the paper commences.

In these tables, column *A* gives the number of the experiment in the series. *B* contains the observed galvanometer deflections when the magnet was inactive; *C*, deflections when the magnet was excited. *D* and *E* contain averages of the groups given in *B* and *C*. At the foot of the table is given the general average, and the deduced percentage variation.

Table I. Magnetic force perpendicular to the plates of the condenser. Two condensers used, each consisting of 11 disks of copper 8 cm. in diameter, with plates of mica between them. In this series the condenser which had the greatest normal capacity was placed between the poles of the magnet. An increase in the differential deflection of the needle when the magnet was excited indicates an increase of capacity in this condenser.

TABLE I.

<i>A.</i>	<i>B.</i>	<i>C.</i>	<i>D.</i>	<i>E.</i>
1	18			
2	19			
3	18			
4	18		18½	
5	....	22		
6	....	22		
7	....	22		
8	....	20		
9	....	22		
10	....	20		
11	....	22		
12	....	20	....	21
13	18			
14	18			
15	18			
16	19	....	18½	
17	....	22		
18	....	20		
19	....	22		
20	....	20	....	21

TABLE II.

<i>A.</i>	<i>B.</i>	<i>C.</i>	<i>D.</i>	<i>E.</i>
1	30			
2	31	....	30½	
3	....	28		
4	....	28	....	28
5	33			
6	32	....	32½	
7	....	28		
8	....	28	....	28
9	35			
10	34	....	34½	

Table II. Exchanged the places of the condensers used in Table I., the smaller of the two being now placed between the poles of the magnet. Direction of the magnetic force as in Table I. In this series a diminished differential deflection of the needle with the excitement of the magnet shows an increase of capacity in the condenser between the poles.

In Series I. and II. the distance between the poles of the magnet was not observed. These distances probably were not the same, for the pole pieces were removed in changing condensers.

Tables III. and IV. Magnetic force perpendicular to the plates of the single condenser. This was made of two disks of copper eight

TABLE III.

A.	B.	C.	D.	E.
1	47			
2	48			
3	47			
4	47		47.2	
3	....	46		
4	....	49		
5	....	47½		
6	....	49½		
7	....	48½	....	48.1
8	49			
9	—			
10	47			
11	45½			
12	—			
13	46	....	46.9	
14	....	49		
15	....	51		
16	....	49		
17	....	51		50
18	50			
19	49			
20	51	....	50	
21	....	53		
22	....	53	....	53
24	51½			
25	52	....	51.7	
26	....	55		
27	....	56	....	55.5
28	52½			
29	53	....	52.7	
Average . . .			49.7	51.6
Increase of capacity, 3½ per cent.				

TABLE IV.

A.	B.	C.	D.	E.
1	51			
2	54			
3	54			
4	54	....	53.2	
5	....	56		
6	....	56		
7	....	56	....	56
8	54			
9	54	....	54	
10	....	55		
11	....	55		
12	....	55½	....	55.1
13	53½			
14	53½	....	53	
Average . . .			53.4	55.5
Increase of capacity, 3½ per cent.				

centimeters in diameter, with a sheet of mica between them. Between the two series of experiments the direction of the magnetic force was reversed. An increase of capacity equal to 3½ per cent is shown in both tables. Hence we conclude that the change in capacity is not reversed in sign with the reversal of the direction of the magnetic force.

Tables V., VI., and VII. show the variation of this effect with the intensity of the field. In Table V. the poles were 1 mm. apart; in Table VI.,  $2\frac{3}{4}$  mm.; in Table VII.,  $4\frac{1}{2}$  mm. distant from each other.

TABLE V.

A.	B.	C.	D.	E.
1	167			
2	166	....	166.5	
3	....	197		
4	....	202	....	199.5
5	175			
6	175	....	175	
Average . . .			170.7	199.5
Increase of capacity, 17 per cent.				

TABLE VI.

A.	B.	C.	D.	E.
1	196			
2	193	....	194.5	
3	....	217		
4	....	218	....	217.5
5	190			
6	196	....	193	
Average . . .			193.7	217.5
Increase of capacity, 12 per cent.				

TABLE VII.

A.	B.	C.	D.	E.
1	177			
2	185	....	181	
3	....	194	....	192
4	....	190		
5	191	....	191	
6	....	197		
7	....	203	....	200
8	193			
9	185	....	189	
Average . . . . .			187	196
Increase of capacity, 5 per cent.				

The single condenser used was made of four sheets of tinfoil 6 cm. by 6 cm., with paraffined paper between them. The direction of the magnetic force as in the preceding tables. The capacity was increased in each series; in Table V. about 17 per cent, in Table VI. 12 per cent, and 6 per cent in Table VII.

Tables VIII. and IX. show results obtained by using a single condenser, whose plates were parallel to the lines of magnetic force. The condenser was made of forty copper strips, 6 mm. wide and 6 cm. long,

TABLE VIII.

A.	B.	C.	D.	E.
1	32			
2	32		32	
3	....	30		
4	....	27½	....	28.8
5	33			
6	33		33	
7	....	32		
8	....	33	....	32.5
9	32			
10	28			
11	33			
12	37			
13	34		34.7	
14	....	37		
15	....	35		
16	....	33	....	35
17	38			
18	38		38	
19	....	37		
20	....	35		
21	....	36	....	36
22	38½			
29	37½			
30	37½		37.8	
31	....	37½		
32	....	35		
33	....	37½	....	36.6
34	38½	....	38.5	
Average . . .			35.7	33.8
Decrease in capacity, 5 per cent.				

TABLE IX.

A.	B.	C.	D.	E.
1	71			
2	70			
3	69			
4	67	....	69.2	
5	....	65		
6	....	66		
7	....	68		
8	....	68	....	66.7
9	72			
10	73			
11	71			
12	74	....	72.2	
Average . . .			70.7	66.7
Decrease in capacity, 5 per cent.				

insulated by paraffined paper. The poles of the magnet were 10 mm. apart. In both of these tables the establishment of a magnetic field is seen to produce a diminution in the capacity of the condenser of about 5 per cent.

A series of experiments (see Table X.) made with a mica condenser, placed in the field with its plates perpendicular to the lines of magnetic force and with the poles 10 mm. apart, showed that its capacity was increased by about 5 per cent.

TABLE X.

A.	B.	C.	D.	E.
1	83			
2	80	....	81	
3	....	88		
4	....	93	....	90
5	91			
6	90	....	91	
7	....	96		
8	....	97	....	96
9	93			
10	92	....	92	
11	....	100		
12	....	100	....	100
13	98			
14	92	....	95	
Average . . .			90	95
Increase of capacity, 5+ percent.				

It is very difficult in such an investigation to prove the absence of error. It would also seem to be nearly as difficult to imagine a source of error which should reverse its sign, as in Tables III. and IV., when two condensers change places, and yet give consistent results showing an increase of capacity in both cases, — which should also show a change of sign when we pass from the use of condensers whose plates are perpendicular to the lines of force to those whose plates are parallel to those lines, — and, finally, which should change in amount with the intensity of the field.

## VIII.

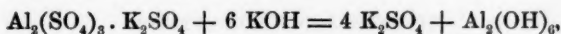
CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.A. THERMOCHEMICAL ANALYSIS OF THE REACTION  
BETWEEN ALUM AND POTASSIUM HYDRATE.

By A. V. E. YOUNG.

Communicated by the Corresponding Secretary, June 10, 1885.

## PART I.

IN the course of a thermochemical study of potassic aluminate I desired to use as one element of calculation the amount of heat evolved in the following reaction,



assuming in accordance with Thomsen's statement that the alum is equivalent, for this purpose at least, to aluminic sulphate. This quantity is given by Thomsen\* as 30528 calories. He determines it directly by precipitation with potassic hydrate in the calorimeter, and, as a control, determines the heat of precipitation with three molecules of baric hydrate. The results of the two methods agree fairly well. This value is made by the same author the basis for the indirect determination of the formation heat of the chloride and several other compounds of aluminum, and this, notwithstanding the fact that he notes the complete precipitation of the aluminic oxide by five molecules of potassic hydrate instead of six, which would appear to indicate the formation of a basic precipitate. He evidently assumes that the addition of six molecules of the hydrate leaves the precipitate free of sulphuric acid, and that the agreement with the result obtained when baric hydrate is used affords confirmation of the assumption. Indeed, in other instances, e. g. sulphates of copper, cobalt, and cadmium, when the two methods do not give concordant results, he adopts the result by baric hydrate, and rejects that by potassic hydrate as being untrustworthy by reason of the formation of a basic precipitate. It would seem unsafe to assume, without experimental verification, that baric

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\* See Thermochemische Untersuchungen, i. 366.

hydrate may not produce a basic precipitate as well as potassic hydrate, and thus render both methods open to the same objection.

However this may be, the results which I obtained soon led to the suspicion that the reaction with potassic hydrate was not so simple as is indicated by the above equation. One question after another arising which I was unable to answer, I have been led step by step to what may be called a thermochemical analysis of the reaction in question. The first part of the results obtained constitutes the substance of the following paper. At a later date, I hope to publish a determination of the precipitation heat of aluminic hydrate by a method free from these objections. The first series of experiments involves the determination of the reaction heat of alum and potassic hydrate, the proportion of the latter present varying from .5 to 10 molecules. This is followed by a parallel series determining the composition of the precipitates obtained in the calorimetric experiments. Before considering in detail the results of the first series, I give a brief description of the calorimetric methods and of the calculations that were used.

#### METHOD AND CALCULATIONS.

The general method of heat measurement is that described by Berthelot. The calorimeter used was made after the specifications given by him\* without essential variation. The inner platinum calorimeter has a capacity of somewhat more than 1,200 c.c. The stirrer is a simple one, a piece of platinum foil fused to a glass rod. The thermometers were made by Baudin of Paris especially for thermochemical work after specifications by Berthelot,† and were calibrated by Pernet at the Bureau International des Poids et Mesures. The zero points have been recently redetermined. The three pairs of duplicates taken together give a range of temperature from 0° to 33° C. They are graduated to fiftieths of a degree, and the readings were made, usually with the aid of a small hand lens, to  $\frac{1}{250}$  of a degree, and often to  $\frac{1}{400}$ . The experiments were performed in a large basement room without artificial heat, where, during a portion of the year at least, the temperature conditions were fairly satisfactory. The operation consisted, with but one or two exceptions, in mixing in the calorimeter two portions of liquid of 500 c.c. For this measurement two flasks were used, their graduation being verified by weight.

Solutions containing the requisite quantity of constituents were prepared, diluted to somewhat less than 500 c.c., and allowed to stand in

\* *Essai de Mécanique Chimique*, i. 140.

† *Ibid.*, p. 164.

closed flasks beside the calorimeter until the following day, or perhaps during a longer interval. When ready for the calorimetric determination one of the prepared solutions was transferred with rinsing to the measuring-flask, (care being taken not to change unduly its temperature in the handling,) and filled to 500 c.c. with distilled water that had stood a day or longer on the same table. It was then poured into the calorimeter and its temperature taken, after thorough stirring, at intervals of five minutes. The change of temperature during this interval should not be more than  $.02^{\circ}$ . At the same time, the second solution having been transferred to the second measuring-flask, its temperature in the flask was taken by a second thermometer in similar manner. Its change likewise should not be more than  $.02^{\circ}$  per interval of five minutes; and it is also important that it should be close to that of the room, which was read from an ordinary thermometer.

When the temperature conditions were satisfactory, and the readings duly recorded, the contents of the second flask were poured as quickly as possible into the calorimeter, the mixture thoroughly stirred, and the resultant temperature recorded. The interval between the last reading of the initial temperatures and the first of the resultant temperature was in this series of experiments one and a half or two minutes, and with few exceptions the maximum temperature was reached in this time. Readings were then taken, always with stirring, every minute for about five minutes, and then at an interval of five minutes, in order to have a record of the rate of cooling.

There seems to be one unsatisfactory point in this method of manipulation; namely, the difficulty of obtaining the true temperature of the second volume of liquid while it still remains in the flask, and of transferring it to the calorimeter without consequent change. Experience will convince one of this difficulty in experiments where a variation of  $.01^{\circ}$  is of considerable importance. My habit is to close the flask and shake it as thoroughly as possible before inserting the thermometer, and to see that its temperature at the time shall be such that it need not be left more than five or ten minutes before transferring to the calorimeter. Meantime the flask stands in a loose bag of flannel, supported by a frame that serves as handle so that the hand itself is distant several inches from the flask. Nevertheless, I have not infrequently obtained apparently accidental results, which varied from the mean notably more than the average variation, and of which the difficulty just described seems the probable cause. I hope later on to reduce, if not to eliminate, this uncertainty by a simple modification of apparatus.

*Calculations.*—The unit of heat employed, the calorie, is the quantity required to raise one kilogramme of water one degree at the temperature of the experiment. The mean temperature after mixing is calculated by the following formula :

$$T_m = \frac{(A + d) T_a + B (T_b - t)}{A + d + B};$$

in which

$T_m$  = mean temperature.

$A$  = water equivalent in grammes of solution A in calorimeter.

$d$  = water equivalent in grammes of calorimeter, stirrer, and thermometer.

$B$  = water equivalent in grammes of solution B.

$T_a$  = observed initial temperature of solution A in calorimeter.

$T_b$  = observed initial temperature of solution B in flask.

$t$  = correction in degrees to make the reading of the two thermometers correspond.

The temperatures  $T_a$  and  $T_b$ , recorded in the tables, are those actually observed. In the calculation of  $T_m$  the correction  $d$  is used, but no correction is made for difference between the observed zero and the actual zero, as it would not affect the final result. The temperature recorded as  $T_c$  is the difference between the calculated mean temperature and the resultant temperature; in other words, the change of temperature due to the reaction, and is positive unless otherwise specified.

The column  $f$  in the tables gives the factor by which  $T_c$  is multiplied to reduce the heat disturbance of the reaction in calories to molecular proportions, and  $H$  is this final result. The factor  $f$  is obtained as follows :

$$f = (A + B + d) \times \frac{\text{mol. wt.}}{\text{grms. taken}} (\text{of alum}).$$

In all the experiments of this paper the water equivalent of the calorimeter and its belongings is 8.5 gm., while  $A$  and  $B$  are the volumes in cubic centimeters of the constituent solutions reckoned as grammes of water (Berthelot's method of calculation\*), each numerically equal to 500 c.c. unless otherwise specified.  $t = .008^\circ$ .

*Limit of Error.*—The reading of temperature is by far the most considerable element limiting the certainty of experimental observation. The quantity of alum used, 20.667 gm., is weighed to one

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\* Essai de Mécanique Chimique, i. 190.

part in more than twenty thousand. The KOH solution is titrated against oxalic acid, and its titration confirmed gravimetrically. The quantity used in an experiment varied from 10.67 c.c. to over 200 c.c. This was measured in a burette to .05 c.c., which would make the maximum variation considerably less than one per cent of the quantity measured, even when the latter was at its minimum. Whereas, if we put the limit of temperature reading at  $.005^{\circ}$ , and consider that the change in temperature depends upon three separate readings, the maximum of error should be  $.01^{\circ}$ , or  $.005^{\circ}$  putting the limit of reading at  $.0025^{\circ}$ . This would be a very large per-cent variation in many of the experiments when the quantity measured falls considerably below  $1^{\circ}$ . Inspection of the tabulated data will show that in many cases the observed variation of  $T_e$  is much smaller than the calculated maximum; e. g. the first six experiments of Table I., where it is only  $.001^{\circ}$ . In most of the experiments a variation of  $.005^{\circ}$  in  $T_e$  makes a variation of .24 Cal. in  $H$ .

#### SERIES I.

The numerical data of these experiments are recorded in Table I. The alum used was the commercial article, well crystallized and free of iron. Of it 20.067 grm. were used in each experiment, and the solution prepared as already described. The proportion of water was about 2,600 molecules to one of alum; in Thomsen's experiments, 2,400. In column  $h$  is recorded the rate of heat disturbance per molecule of KOH. The results  $H$  and  $h$  are seen graphically expressed in Plate I., where  $x$  is the number of molecules of KOH added, and  $y$  in Line I. represents  $H$ , in Line III.,  $h \times 10$ .

Inspection of Line I. shows that the heat evolution increases with the quantity of KOH, reaching a maximum at  $x = 6$  or  $6.5$ , and from this point diminishes until  $x = 10$ , when the re-solution of the precipitate in the excess of KOH is complete. This means that the solution of the precipitate in excess of KOH is accompanied by heat absorption, or is endothermic. It will be shown farther on that the addition of KOH beyond  $x = 8.5$  causes no further heat disturbance, and that 8.13 mol. KOH completely redissolve the precipitate; hence, in constructing the line, the value of  $y$  at  $x = 8.13$  is made the same as at  $x = 10$ .

Line III. reveals still more. It shows a constant rate of heat evolution per molecule of KOH from  $x = .5$  to  $x = 1$ . At this point it drops abruptly. Now in the analytical part it will be shown (see Plate II. Line V.) that precipitation begins between  $x = 1$  and

$x = 1.5$ , probably at  $x = 1.13$ . Hence, in constructing Line III. the minimum is put hypothetically at  $x = 1.13$ , instead of at  $x = 1.5$  which is the point actually determined. Inasmuch as the precipitate at first produced redissolves in excess of alum up to  $x = 1.13$ , the drop in the line at this point indicates probably that this re-solution also is accompanied by heat absorption. This will be evident upon considering that the heat disturbance,  $h$ , is a positive resultant, made up of both positive and negative elements. The principal positive element is the formation heat of potassic sulphate, and since this in all probability remains approximately constant for equal portions of KOH entering into combination, it follows that the negative element increases at the point  $x = 1.13$  in consequence of precipitation. In other words, precipitation is accompanied by heat evolution, and re-solution of the precipitate by heat absorption.\*

Beyond  $x = 1.13$  there is evidently a tendency to rise slightly up to  $x = 5$ , or thereabouts. The break at  $x = 4.8$  is within the limit of error, since the larger value recorded in Table I. gives the alternative point,  $x = 4.8$ , just above the line as seen in the plate. Indeed, the increase between  $x = 1.13$  and  $x = 5$  depends upon differences which lie so close to the limit of experimental error that one must hesitate to consider it more than probable. It would be interesting to establish it beyond doubt, in view of the analytical results shown in Plate II., Line VII. There can be no doubt, however, that the line drops beyond  $x = 5.12$ , as would be expected.

It is to be noted that the maximum in Line I. occurs at  $x = 6$  or  $6.5$ ; while in Line III. it occurs at  $x = 5$ , which is the point at which the aluminic oxide is completely precipitated. This leads to the question, What causes the continued heat evolution after the precipitation is total? the discussion of which must be deferred until the analytical results have been described. The three experiments recorded in Table III. serve, however, to fix one point bearing thereon. 4.8 mol. KOH were added to one of alum in the usual conditions. Then to this mixture were added in the calorimeter the remaining 1.2 mol. KOH, in the proportionate quantity of water, and the heat evolution measured. The results are fairly satisfactory, considering that the necessary conditions of the experiments were not the best for calorimetric measurement. They serve to show, at least, that the continued evolution of heat between  $x = 4.8$  and  $x = 6$ , in Series I., may be accounted for by the action of the 1.2 mol. KOH on the

\* See similar case of lead, Thomsen, i. 377.

precipitate formed by the 4.8 mol. A previous experiment, made by adding KOH in the calorimeter to the liquid portion of the mixture 1 alum + 5 KOH (the precipitate being removed), gave zero for a result.

### SERIES II.

In the second series of experiments the same quantity of alum was dissolved, 10 mol. KOH added, and the whole made up to 500 c.c., as in Series I. To this was added in the calorimeter 500 c.c. of sulphuric acid solution, containing of  $\text{H}_2\text{SO}_4$  quantities varying from .5 to 3 molecules. The numerical data are recorded in Table II. It will be seen that the rate of heat disturbance per molecule of  $\text{H}_2\text{SO}_4$  is practically constant for  $n = .5$  and  $n = .75$ , but increases at  $n = 1$ ; the first precipitation by neutralization of KOH occurs between  $n = .75$  and  $n = 1$ . The rate then increases to  $n = 2.2$ , when it again drops. Instead of expressing these direct results graphically, I have calculated from them (at least from Exp. 42-48) the corresponding points in the Lines I. and III. The possibility of this calculation will be apparent from considering that  $H$  in Series II. is the formation heat of potassic sulphate plus or minus the heat disturbance involved in separating the equivalent potassic hydrate from whatever form of combination it may be in before the addition of sulphuric acid. If we assume that the  $n$  mol.  $\text{H}_2\text{SO}_4$  (from  $n = 1.5$  to  $n = 2.2$ ) are converted into  $\text{K}_2\text{SO}_4$ , and count the formation heat of the latter as a known quantity, we have the means of calculating indirectly the values of  $y$  in Series I. for  $x = 6, 7$ , and  $10$ . These values locate the supplementary Lines II. and IV., Plate I. They are separated by a small and approximately constant quantity from the Lines I. and III.

A similar discussion of the values for  $n = .5$  and  $.75$  will make evident whether or not the addition of KOH beyond 8.13 mol. has any effect. The formation heat of  $\text{K}_2\text{SO}_4$  is according to Thomsen 31.288 Cal. One half of this, 15.644 Cal., is larger by .96 than the mean result of Exp. 36-39, Series II., which would indicate that heat was absorbed in liberating KOH from its previous state of combination, and hence that the combination of the 9th and 10th mol. in Series I. was accompanied by heat evolution. This, if true, would be an interesting fact; but the question arises, May not the formation heat of  $\text{K}_2\text{SO}_4$  in Exp. 36-39 be less than 31.288 Cal., this value having been determined for a degree of concentration six times as great? I therefore determined it independently, using, first, the same quantities of KOH and  $\text{H}_2\text{SO}_4$  as occur in the reaction  $n = .5$ , and

then six times their quantities, the volume 1,000 c.c. remaining the same throughout. In the last case, the proportion is about the same as in Thomsen's experiment. The data are shown in Table IV. At the degree of concentration which corresponds to Exp. 36-39, the formation heat of  $\frac{1}{2}$   $\text{K}_2\text{SO}_4$  is found to be (Exp. 57-61) 14.63 Cal., which agrees with  $H$  in Exp. 36-39; while for one sixth this dilution  $H$  is found to be 31.26 or 15.63 for  $\frac{1}{2}$   $\text{K}_2\text{SO}_4$ ; Exps. 53, 54, correspond to Thomsen's conditions.

This proves that the second half of the 9th mol. and the 10th mol. in Series I. are not in chemical combination, or, at least, that there is no evidence of it in the thermal phenomena. In other words, the heat disturbance ceases when 8.13 mol. KOH have been added, as indicated in Line I., Plate I.

As dilution was found to affect the determination of the formation heat of  $\text{K}_2\text{SO}_4$ , it became desirable to test its influence upon the resultant  $H$  of Series I., in which this formation heat is the principal element. To do this the reaction heat of 6 mol. KOH on 1 of alum was determined, the absolute amount of substance undergoing change in the standard volume, 1,000 c.c., being only one fourth the quantity used in Exp. 23-26, Series I. These data are recorded in Table V. The mean result of the five experiments is 29.26 Cal., in place of 30.66 by the previous experiments.

It seems not improbable, in view of these facts, that the tendency of the Line III., Plate I., to rise between  $x = 1.5$  and  $x = 5.1$ , may be due to the increase in the amount of substance undergoing change in the unit of volume.

The complexity of the thermochemical results thus far described made evident the necessity of a sharper definition of the chemical changes actually taking place in the calorimeter. The study of these constitutes the second part of this paper.

## PART II.

*General Method.*—It would seem that the most direct method of obtaining evidence as to the exact chemical change would be to determine the composition of the various precipitates produced in the calorimetric experiments. The impossibility, however, of washing them without changing their composition, indicated rather the analysis of the filtrate from them as the preferable method. Either one determines only the total change in the distribution of constituents between the soluble and insoluble portions of the system.

The method pursued was the following: 50 c.c. of alum solution, containing five grammes of the crystallized salt, were made up to a little less than 125 c.c. The required quantity of KOH solution was also made up to about the same volume. These two solutions were then thoroughly mixed, the volume of the mixture made up accurately to 250 c.c. ( $T\ 20^{\circ}\text{C.}$ ), again well shaken, and thrown upon a dry filter, the filtration being hastened in some instances by using the pump. From the filtrate separate portions of 50 c.c. each were taken, in which were made duplicate determinations of  $\text{SO}_3$  and  $\text{Al}_2\text{O}_3$ , and in several instances of  $\text{K}_2\text{O}$ . The  $\text{SO}_3$  was determined, of course, by precipitation with  $\text{BaCl}_2$ ; the  $\text{Al}_2\text{O}_3$ , by precipitation with  $\text{NH}_3$ ; and the  $\text{K}_2\text{O}$  was weighed as sulphate after the removal of  $\text{Al}_2\text{O}_3$ . The proportion of constituents and water is the same as in the calorimetric experiments, the scale being simply reduced to one fourth.

Analyses somewhat similar have been made by S. U. Pickering\* of the precipitates obtained from aluminic sulphate by addition of varying quantities of  $\text{Na}_2\text{CO}_3$ . His method was to determine the  $\text{SO}_3$  and  $\text{Al}_2\text{O}_3$  in the precipitate itself after thorough washing, although he recognized the fact that its composition was changed by the operation. This would be a serious objection to the use of this method for the purposes of this investigation, although less so in his experiments undertaken from a different standpoint. Our results, so far as they cover the same points, do not conflict in the general direction of their indications, although quantitatively they differ somewhat.

Mills also has determined simply the amount of  $\text{Al}_2\text{O}_3$  precipitated from alum solution by varying quantities of  $\text{Na}_2\text{CO}_3$ .†

It should be noted that the method of this investigation gives no evidence as to the degree of hydration of the precipitate; that point I am obliged to pass by.

In the first experiment of this series (Exp. A) the method was applied in blank to a solution of alum, no KOH being added. The results obtained were:

$$\text{Al}_2\text{O}_3 = .1080 \text{ grm.}$$

$$= .1074$$

$$\text{Mean} = .1077$$

$$\text{SO}_3 = .3321 \text{ grm.}$$

$$= .3326$$

$$\text{Mean} = .3324$$

As these correspond to 1 grm. alum taken, multiplying by 100 converts them into per cents. Correcting for the volume of pipettes and

\* Chemical News, xlv. 121, 133, 146.

† Journal of Chem. Society, [2,] xli. 341.

flask makes them respectively 10.90 and 33.64. Adding to these the determinations of  $K_2O$  and  $H_2O$ , made by separate experiments, makes the complete analysis of the alum used as follows:

	Found.	Cal.
$Al_2O_3$	10.90	10.76
$SO_3$	33.64	33.75
$K_2O$	9.94	9.93
$H_2O$	45.64	45.56
	<hr/> 100.12	<hr/> 100.00

It is evident that the difference between the results of A and of corresponding results of subsequent experiments in which precipitation does occur, gives the amount of  $Al_2O_3$  and  $SO_3$  in the precipitate. The final results of each experiment are reckoned as parts of  $Al_2O_3$  in 100 parts of anhydrous precipitate, and as parts of  $Al_2O_3$  precipitated out of 100 parts of  $Al_2O_3$  present in the total system. The following is an example of a calculation in full:—

	$Al_2O_3$ .	$SO_3$ .
A =	.10766 grm.	.33231
D =	.0689	.31134
Precipitate =	<hr/> .03876	<hr/> .02097

$$\text{Anhydrous precipitate} = \frac{.03876 \times 100}{.03876 + .02097} = 64.89\% \text{ } Al_2O_3.$$

$$Al_2O_3 \text{ of precipitate} = \frac{.03876 \times 100}{.10766} = 36.00\% \text{ of total } Al_2O_3.$$

The data of this series of experiments are recorded in Table VI. The quantity of KOH varies, as will be seen, from 1.5 to 8 molecules.

Before discussing the results, I describe another series made to reverse, as it were, the conditions of the former.

Fifty c.c. of alum solution were taken as before, and to this ten molecules KOH added, and the whole made up to a little less than 125 c.c. Sulphuric acid solution, containing quantities of  $H_2SO_4$  proportional to 1.5, 2, 2.5, and 4 molecules, was added, and the mixture brought accurately to 250 c.c. ( $T$   $20^\circ$ ), thoroughly shaken, filtered, and the filtrate analyzed as usual. The only variation was in Exp. *T*, when 5 mol. HCl were used in place of 2.5  $H_2SO_4$ , and this will be more particularly discussed in a subsequent publication. The data of these experiments are recorded in Table VII.

The calculation of the composition of the precipitate is similar to that in the preceding series, except that account must be taken of the  $\text{SO}_3$  added.

In three experiments, viz.  $H$ ,  $T$ , and  $S'''$  (in  $H$  and  $T$  the total amount of precipitate was at its maximum), the  $\text{K}_2\text{O}$  in the filtrate was determined. The full calculated amount being found, it was deemed unnecessary to determine it at other points, since it evidently formed no part of the precipitate.

*Discussion.*—The results of the first two series are graphically expressed in Lines V., VI., VII., and VIII., Plate II. In Line V.,  $x$  = number of molecules of  $\text{KOH}$  added, and  $y$  = per cent of total  $\text{Al}_2\text{O}_3$  found in the precipitate. While in Line VII.,  $x$  = the same, but  $y$  = parts of  $\text{Al}_2\text{O}_3$  in 100 parts of anhydrous precipitate. Continuing Line V. beyond  $x = 1.5$  and  $x = 8$  toward the axis of  $x$  indicates  $x = 1.13$  and  $x = 8.13$  as the probable points respectively of initial and final precipitation. The line reaches its maximum at  $x = 4.8$ , making the precipitation of the  $\text{Al}_2\text{O}_3$  complete at this point.

Line VII. shows that the first precipitate is the least basic, containing only 64% of  $\text{Al}_2\text{O}_3$ ; that from  $x = 1.5$  to  $x = 4$  there is apparently a slight increase of basicity, but that from  $x = 4$  to  $x = 4.8$  the increase is more rapid; that between  $x = 4.8$  and  $x = 6$  the rapidity of change is still greater; that at  $x = 6$  it drops back again, leaving a precipitate free of  $\text{SO}_3$  at  $x = 7$ . It will be noticed that  $x = 4.8$  and  $x = 6$  are salient points in these lines, as they are in Lines I. and III., expressing the thermal phenomena.

The points in Line VI.,  $x = 5, 6$ , and  $7$ , are obtained from Exp.  $N$ ,  $O$ , and  $T$ , by making  $x$  the number of molecules of  $\text{KOH}$  left unneutralized by the  $\text{H}_2\text{SO}_4$  added. It will be seen that they approximate closely to the corresponding points in Line V., the difference being probably within the limits of experimental error. This evidently means that, when the same amount of free  $\text{KOH}$  is present, the same precipitate is obtained, whether it come from adding  $\text{KOH}$  to alum, or from neutralizing the excess of  $\text{KOH}$  in the alkaline solution of  $\text{Al}_2\text{O}_3$  obtained by adding 10  $\text{KOH}$  to alum. This result was unexpected, and suggested at once the possibility of a chemical equilibrium existing between the constituents of the soluble and of the insoluble portions of the system. To test this idea, Exp.  $P$  was made, using 4 mol.  $\text{H}_2\text{SO}_4$ . Assuming that 4 mol.  $\text{KOH}$  out of the ten added are uncombined with  $\text{H}_2\text{SO}_4$ , the 4 mol.  $\text{H}_2\text{SO}_4$  now added would neutralize them, leaving an excess of 2 mol.  $\text{H}_2\text{SO}_4$ , and making a system, neglecting the  $\text{K}_2\text{SO}_4$  constituted of 1 mol.  $\text{Al}_2\text{O}_3$  and 2  $\text{H}_2\text{SO}_4$ , the

same which we suppose to exist when 2 mol. KOH are added to 1 mol. alum. Putting  $x = 2$ , therefore, the results of Exp. *P* give the points *P* in the Lines VI. and VIII., which approach at least the corresponding points in V. and VII. Regarding this as a further indication of an equilibrium, I varied the experiment in the following manner (Exp. *Q*): The usual 50 c.c. of alum solution were taken, 6 mol. KOH added, and the whole made up to 250 c.c. Another portion of 50 c.c. alum solution was then taken, and made up to nearly 250 c.c. The two solutions thus prepared were then mixed, made up to 500 c.c., thoroughly shaken, filtered, and portions of 50 c.c. taken from the filtrate for analysis, as usual. The total system here is evidently the same in the proportion of its constituents (water included) as would be obtained by mixing 1 mol. alum and 3 mol. KOH in a volume of 250 c.c. At the same time, we can calculate from Exp. *I*, Table VII., what would be the composition of the precipitate, assuming that it remained the same as produced by 6 mol. KOH in the first mixture, increased only by the remaining 9.47% of the total  $\text{Al}_2\text{O}_3$  of the first portion; the KOH uncombined with  $\text{H}_2\text{SO}_4$  in that portion taking  $\text{SO}_3$  from the second portion of alum, but causing no increase of precipitate since it is equivalent to only about .14 mol. KOH. The precipitate thus calculated would contain 50% of the total  $\text{Al}_2\text{O}_3$  of the system, and have a composition of 95.29%  $\text{Al}_2\text{O}_3$  to 4.71% of  $\text{SO}_3$ . This gives the crossed points *Q* ( $x = 3$ ). But actual analysis of the filtrate gives for the precipitate the results recorded in *Q*, Table VIII., and the points *Q* in the Lines VI. and VIII. This shows that the initial distribution of constituents between the soluble and insoluble portions of the system has changed completely, approaching that obtained by adding to 1 mol. alum 3 mol. KOH. The change in this case consists only in an increase of  $\text{SO}_3$  in the precipitate.

Another experiment was then made (Exp. *R*) by mixing in similar manner (1 alum + 6 KOH) in 250 c.c. and (1 alum + 1.5 KOH) in 250 c.c.; making a total system equivalent to 1 alum + 3.8 KOH in 250 c.c. Calculating as in *Q*, from Exp. *B* and *I*, the initial composition of this mixed precipitate, and on the assumption that the unneutralized .1 mol. KOH of the 6 mol. KOH is added to the 1.5 mol. in the second portion, we obtain the crossed points *R* ( $x = 3.8$ ). Analysis of the filtrate, on the other hand, gives the points *R* ( $x = 3.8$ ) in the Lines VI. and VIII., which likewise shows a very considerable change in the precipitate, and a close approach to the system obtained by adding 3.8 mol. KOH to 1 mol. alum. In this case the change

is more complex than in  $Q$ , consisting in the precipitate acquiring both  $\text{Al}_2\text{O}_3$  and  $\text{SO}_3$ . In other words, the equilibrium has moved the crossed point  $R$  up to the point  $R$  in VI., and the crossed point  $R$  down to  $R$  in VIII.

The results already described indicate unmistakably the existence of the equilibrium; but, to vary the evidence still more, Exp.  $S'$ ,  $S''$ , and  $S'''$  were made, as follows:—

Aluminum was dissolved in KOH solution and the KOH exactly neutralized by HCl, independent experiments having proved that the precipitate thus obtained is free of acid. The volume of this mixture having the freshly precipitated hydrate in suspension was brought up to 250 c.c. Fifty c.c. of alum solution ( $= 5$  grm. alum) were then added, the whole made up to 500 c.c. and thoroughly mixed. Before filtering, portions of 50 c.c. each were withdrawn with a pipette, care being taken to insure the uniform distribution of the suspended precipitate by constant stirring. In these portions the precipitate was redissolved by HCl and the total  $\text{Al}_2\text{O}_3$  of the system determined. The remainder of the mixture was filtered as usual, and portions of 50 c.c. of its filtrate taken for the usual determinations of  $\text{SO}_3$  and  $\text{Al}_2\text{O}_3$ . The differences between the total  $\text{Al}_2\text{O}_3$  and  $\text{SO}_3$  and the  $\text{Al}_2\text{O}_3$  and  $\text{SO}_3$  found in the filtrate give the composition of the precipitate. In  $S'$  the amount of  $\text{Al}_2\text{O}_3$  added as precipitate was 1.12 times that added as alum, making a proportion of 2.12 mol.  $\text{Al}_2\text{O}_3$  to 3 mol.  $\text{SO}_3$  in 500 c.c. of volume; equivalent to 1  $\text{Al}_2\text{O}_3$  and 1.4  $\text{SO}_3$  in approximately 250 c.c. This so far as relation between  $\text{Al}_2\text{O}_3$  and  $\text{SO}_3$  is concerned, should be equivalent to 1 alum + 3.2 KOH. Using therefore the analytical results of  $S'$ , Table VIII., and making  $x = 3.2$ , we obtain the dotted points  $S'$ , Plate II., approximating closely to the values otherwise obtained; whereas had the precipitate remained unchanged it would have been 100%  $\text{Al}_2\text{O}_3$  and contained 52.82% of the total  $\text{Al}_2\text{O}_3$ . These values are represented by the crossed points  $S'$ . The change consists mainly in acquiring  $\text{SO}_3$ .

Exp.  $S''$  is similar, the only variation being in the quantity of precipitated  $\text{Al}_2\text{O}_3$  added. The results are shown in the points  $S''$  ( $x = 2.5$ ); whereas the crossed points  $S''$  indicate what would have been the results had the precipitate remained unchanged. Here, too, the change is in acquiring  $\text{SO}_3$ .

Still another experiment,  $S'''$ , was made, varying again the quantity of  $\text{Al}_2\text{O}_3$  added. The actual results are shown in the points  $S'''$  ( $x = 2$ ), and the initial precipitate in the crossed points,  $S'''$ . Here it is apparent that the change consists in gaining  $\text{SO}_3$  and losing  $\text{Al}_2\text{O}_3$ .

The proof of equilibrium is indubitable, the initial precipitate gaining or losing  $\text{Al}_2\text{O}_3$  or  $\text{SO}_3$  as may be necessary to bring about the characteristic distribution of constituents for the given conditions. It is also apparent that  $\text{K}_2\text{SO}_4$  plays no part, and may be considered as practically outside the system, since its presence in quantity varying from less than one molecule to more than ten molecules has not disturbed the leading phenomenon.

Another fact may be noted here. The corresponding points in the Lines V., VI., VII., and VIII., that lie to the right of  $x = 5$ , approximate closely, probably within the limits of experimental error. To the left of  $x = 5$ , the divergence is greatest, but the difference in every instance lies on the side of approach to the Lines V. and VII. from the initial points, never going beyond. The probable explanation of this lies in the fact that, in all the experiments yielding the Lines V. and VII., also the points of the other lines to the right of  $x = 5$ , the system in its initial state is homogeneous. While in the remaining experiments, with the single exception of Exp. P, it is non-homogeneous (liquid and solid). It is not strange, then, that this non-homogeneity exercises a retarding influence upon the equilibrium. It is rather a matter of surprise that it should not prove more of an obstacle than it does.

*Effect of Temperature, Time, and Dilution on the Equilibrium.*

Temperature often exerts an influence in reactions such as we have been describing, and to test its effect in this instance is the object of the three following experiments,  $E'$ ,  $E''$ , and  $E'''$ . In the first place two successive experiments were made as nearly alike as possible, in order to measure the probable variation in the final results of a single experiment. I give the details in full. The solutions were prepared in the usual manner, 4 mol. KOH being added to 1 mol. alum. The temperature of the room in both experiments was about  $23^\circ \text{C}$ ., but the contents of flasks before bringing up to standard volume and before taking out portions of 50 c.c. were cooled, as in previous experiments, to  $20^\circ$ . The results were as follows:—

	$E'$		$E''$	
	$\text{Al}_2\text{O}_3$	$\text{SO}_3$	$\text{Al}_2\text{O}_3$	$\text{SO}_3$
Found in 50 c.c. I. =	.0174 grm.	.28221	.0159	.28203
II. =	.0174	.28210	.0162	.28190
Mean =	.0174	.28216	.0161	.28197

<i>E'</i> .		<i>E''</i> .	
$\text{Al}_2\text{O}_3$ .	$\text{SO}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{SO}_3$ .
$A = .10766$ gram.	.33231	.10766	.33231
$E' = .0174$	.28216	.0161	.28197
Precipitate = .09026	.05015	.09156	.05034

Anhydrous precipitate = 64.28%  $\text{Al}_2\text{O}_3$       64.52%  $\text{Al}_2\text{O}_3$   
    = 35.72%  $\text{SO}_3$       35.48%  $\text{SO}_3$   
 Precipitate = 83.84% of total  $\text{Al}_2\text{O}_3$       85.05% of total  $\text{Al}_2\text{O}_3$

It will be seen that the  $\text{SO}_3$  determinations do not differ appreciably more than the duplicate determinations of  $\text{SO}_3$  in the same solution; while the amounts of  $\text{Al}_2\text{O}_3$  obtained, differ by more than a milligramme, one part in seventeen. So in another instance, .2893 and .2899 gram.  $\text{SO}_3$  were obtained in two experiments entirely distinct from the beginning. It would almost seem that the equilibrium were more sharply defined with reference to  $\text{SO}_3$  than to  $\text{Al}_2\text{O}_3$ . Yet it should be borne in mind that the amounts of  $\text{SO}_3$  actually weighed are always large, .28 gram. or more, while the amounts of  $\text{Al}_2\text{O}_3$  weighed were as low as .01 gram., and hence the experimental determination of  $\text{SO}_3$  is less affected by error than that of  $\text{Al}_2\text{O}_3$ .

The final results being dependent on the ratio between differences, small compared with the quantities actually measured, considerable latitude of variation must be allowed.

The experiment was then repeated, *E'''*, the only variation being that, after the flask was filled to 250 c.c. (at 21°), it was heated to about 50–55° for twenty-five minutes, then turned into a large beaker with glass cover and heated fifteen minutes more, and finally boiled two or three minutes. The liquid on the cover was rinsed off with the solution, and the whole thrown while boiling hot upon a dry filter, which was covered during the ten minutes of filtration. The filtrate was then cooled to 20°, and portions of 50 c.c. taken as usual for analysis. The loss of water by evaporation could not have been great, and would not affect the ratio between  $\text{Al}_2\text{O}_3$  and  $\text{SO}_3$ . The results were:

$\text{Al}_2\text{O}_3$ .	$\text{SO}_3$ .
I. = .0148	.30473
II. = .0148	
Mean = .0148	.30473

This makes a precipitate containing 86.25% of the total  $\text{Al}_2\text{O}_3$ , with a composition of 77.10%  $\text{Al}_2\text{O}_3$  and 22.90%  $\text{SO}_3$ . The precipitate at the temperature of boiling has, therefore, lost considerable  $\text{SO}_3$ , while the ratio of the  $\text{Al}_2\text{O}_3$  precipitated to the total has not much changed.

Exp.  $E^{\text{IV}}$ . A second variation was made to test the influence of dilution on the equilibrium, since many of the experiments already described indicate that water plays a part in the reaction besides that of a mere solvent. Alum and KOH in the same quantity as in  $E'$ ,  $E''$ , and  $E'''$  were mixed, and the solution made up to 1,000 c.c., instead of 250, making the absolute quantity in unit of volume one fourth what it was in the preceding experiments. Of the filtrate, portions of 100 c.c. were taken, instead of 50, and the quantities of  $\text{SO}_3$  and  $\text{Al}_2\text{O}_3$  found were multiplied by two in order to make them comparable with the others. The results were:

	$\text{Al}_2\text{O}_3$ .	$\text{SO}_3$ .
I. =	.0162	.28570
II. =	.0160	.28578
Mean =	.0161	.28574

This indicates a precipitate containing 85.05% of total  $\text{Al}_2\text{O}_3$ , and of composition 66.29%  $\text{Al}_2\text{O}_3$  and 33.71%  $\text{SO}_3$ .

Dilution also has tended to diminish  $\text{SO}_3$  in the precipitate without changing the proportion of  $\text{Al}_2\text{O}_3$  precipitated.

Is the equilibrium a function of time also? To answer this a mixture was prepared (Exp.  $E^{\text{V}}$ ) at the same time as  $E'$ , and in precisely the same manner. But instead of filtering at once as in  $E'$ , the mixture was allowed to stand in a closed flask at the temperature of the room for seven days, and then filtered as in  $E'$ , and the filtrate analyzed. The result was:

	$\text{Al}_2\text{O}_3$ .	$\text{SO}_3$ .
I. =	.0152	.28210
II. =	.0146	.28217
Mean =	.0149	.28214

This makes a precipitate containing 86.12% of the total  $\text{Al}_2\text{O}_3$ , and in composition 64.89%  $\text{Al}_2\text{O}_3$  and 35.11%  $\text{SO}_3$ , or practically the same as in  $E'$ . Here, too, is to be seen the close agreement in quantity of  $\text{SO}_3$  and the greater variation in  $\text{Al}_2\text{O}_3$ .

This experiment was suggested by the fact that the basic filtrates obtained by adding one or more molecules of KOH, and removing the precipitate, yield a second precipitate on standing, the length of time apparently depending on the degree of basicity. This second precipitate is also produced in a few minutes by boiling or by adding a considerable quantity of water. Exp.  $E^V$  is therefore interesting as showing that time does not affect the equilibrium while the original precipitate remains in the system.

#### CONCLUSION.

It is clear, from the evidence herein set forth, that in the reaction which has been the subject of investigation we have another instance of chemical equilibrium or mass reaction, and the question at once arises, What is the cause of it? Without attempting to answer this definitely at present, we suggest the probability that it may be due to the progressive dissociation by water of basic compounds of  $Al_2O_3$  and  $SO_3$  on the one hand, and of potassic aluminate on the other. It would appear from Exp.  $S'$ ,  $S''$ , and  $S'''$ , that  $Al_2O_3 \cdot 3 SO_3$  must itself be partly dissociated in water solution, and it is not improbable that the matter may be still further complicated by the dissociation of another substance formed from the products of decomposition of the first. I hope to obtain definite evidence upon this point, by continuing a line of investigation already begun. That the basic sulphates of alumina are dissociated, is apparently indicated by the fact already cited, that the filtrates in experiments  $B$  to  $H$  yield a second precipitate on heating, diluting, or standing some length of time. While the crystallized potassic aluminate to which Fremy assigns the formula,  $K_2O \cdot Al_2O_3 \cdot 3 H_2O$ , decomposes on the addition of water with the separation of aluminic hydrate.

However that may be, it is evident, (1.) that the reaction between alum and KOH is not by any means as represented in what may be called the ideal equation cited in the beginning of this paper, but that it is much complicated by secondary reactions which render it entirely unsuitable for the determination of the formation heat of the sulphate and other compounds of alumina, although the numerical error introduced by its use may not be great; and (2.) that these secondary reactions are of the nature of chemical equilibriums or mass reactions, the distribution of the constituents of the system about the line of solubility being a function of temperature, volume (i. e. dilution), and total mass of constituents.

TABLE I.

1 Alum +  $n$  KOH. $A = B = 500.$   $d = 8.5.$   $f = 47655.4.$ 

No. of Exp.	$n$ .	$T_a$ .	$T_b$ .	$T_m$ .	$T_c$ .	$H =$ $T_c \times f$ .	$h =$ $H \div n$ .	Mean $H$ .	Mean $h$ .
1	0.5	16.66	17.275	16.96	.060	Cal.	Cal.	Cal.	Cal.
2	0.5	16.4575	17.2225	16.833	.0595	2.86	5.72	2.85	5.69
						2.84	5.67		
3	1.0	16.6675	17.2925	16.973	.1195	5.70	5.70	5.72	5.72
4	1.0	16.57	17.52	17.037	.1205	5.74	5.74		
5	1.5	16.70	17.0675	16.878	.1695	8.08	5.39	8.09	5.39
6	1.5	16.826	17.73	17.27	.1700	8.10	5.40		
7	2.5	17.02	18.073	17.538	.287	13.68	5.47	13.58	5.43
8	2.5	16.6075	17.04	16.818	.283	13.49	5.39		
9	2.5	16.545	17.40	16.965	.285	13.58	5.43		
10	4.5	17.08	17.93	17.497	.513	24.45	5.43	24.42	5.43
11	4.5	16.525	17.16	16.836	.514	24.50	5.44		
12	4.5	17.44	18.255	17.84	.510	24.31	5.40		
13	4.8	16.18	17.0525	16.609	.5335	25.42	5.30	25.79	5.37
14	4.8	17.2125	17.845	17.522	.548	26.12	5.44		
15	4.8	17.37	18.5775	17.965	.535	25.50	5.31		
16	4.8	16.4325	17.80	17.107	.548	26.12	5.44		
17	5.12	17.03	16.92	16.971	.594	28.31	5.53	28.39	5.55
18	5.12	17.06	17.68	17.363	.5945	28.33	5.53		
19	5.12	16.78	17.75	17.257	.5955	28.38	5.54		
20	5.12	16.17	17.0075	16.581	.599	28.55	5.58		
21	5.5	16.69	17.46	17.068	.632	30.12	5.48	30.14	5.48
22	5.5	16.49	17.35	16.912	.633	30.17	5.49		
23	6.0	19.5825	20.15	19.86	.640	30.49	5.08	30.66	5.11
24	6.0	19.84	20.5075	20.167	.633	30.17	5.03		
25	6.0	16.66	17.84	17.241	.6515	31.05	5.18		
26	6.0	16.6925	17.62	17.148	.6495	30.95	5.16		
27	6.5	16.2375	16.8825	16.553	.647	30.83	4.74	30.83	4.74
28	6.5	16.62	17.895	17.248	.6495	30.95	4.76		
29	6.5	16.445	17.705	17.066	.644	30.69	4.72		
30	7.0	19.15	19.72	19.429	.621	29.59	4.23	29.59	4.23
31	10.0	16.9725	18.01	17.483	.617	29.40	2.94	29.27	2.93
32	10.0	16.46	17.84	17.14	.610	29.07	2.91		
33	10.0	16.62	17.74	17.171	.619	29.50	2.95		
34	10.0	19.26	20.34	19.791	.6115	29.14	2.91		
35	10.0	19.1975	20.21	19.696	....	29.22	2.92		

TABLE II.

(1 Alum + 10 KOH) +  $n$  H<sub>2</sub>SO<sub>4</sub>. $A = B = 500.$   $d = 8.5.$   $f = 47655.4.$ 

No. of Exp.	$n.$	$T_a.$	$T_b.$	$T_m.$	$T_c.$	$\frac{H=}{T_c \times f.}$	$\frac{h=}{H + n.}$	Mean $H.$	Mean $h.$
		°	°	°	°	Cal.	Cal.	Cal.	Cal.
36	.50	19.2575	20.49	19.865	.305	14.54	29.07	14.68	29.36
37	.50	19.41	20.445	19.919	.311	14.82	29.64		
38	.75	17.81	19.14	18.465	.4575	21.80	29.07	21.83	29.10
39	.75	17.8175	19.0075	18.404	.4585	21.85	29.13		
40	1.00	18.19	19.5525	18.862	.628	29.03	29.93	30.05	30.05
41	1.00	18.21	19.725	18.957	.633	30.17	30.17		
42	1.50	17.92	18.905	18.107	.998	47.56	31.71	47.39	31.60
43	1.50	17.9675	18.9375	18.444	.991	47.23	31.49		
44	2.00	17.8975	18.98	18.43	1.340	63.86	31.93	63.55	31.77
45	2.00	19.094	19.65	19.366	1.3415	63.93	31.97		
46	2.00	17.605	19.0375	18.311	1.319	62.86	31.43		
47	2.20	17.82	19.0575	18.43	1.4575	69.46	31.57	69.28	31.49
48	2.20	18.22	18.53	18.37	1.450	69.10	31.41		
49	3.00	17.80	18.665	18.225	1.785	85.07	28.36	85.07	28.36

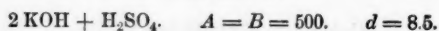
TABLE III.

(1 Alum + 4.8 KOH) + 1.2 KOH.

 $A + d = 1008.5.$   $B = 124.96.$   $f = 47655.4.$ 

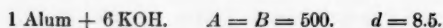
No. of Exp.	$T_a.$	$T_b.$	$T_m.$	$T_c.$	$\frac{H=}{T_c \times f.}$	Mean $H.$
	°	°	°	°	Cal.	Cal.
50	18.08	18.67	18.144	.086	4.10	3.83
51	17.57	17.87	17.602	.073	3.48	
52	17.0475	16.565	16.993	.082	3.91	

TABLE IV.



No of Exp.	$n = \text{grm. of H}_2\text{SO}_4$	$T_a$	$T_b$	$T_m$	$T_c$	$H = T_c \times \frac{1008.5 \times 98}{n = \text{grm. H}_2\text{SO}_4}$	Mean $H$
		°	°	°	°	Cal.	Cal.
53	6.8071	17.6925	18.45	18.064	2.1435	31.12	31.26
54	6.8071	17.64	18.9075	18.264	2.1385	31.05	
55	6.227	14.62	15.43	15.018	1.9895	31.58	29.26
56	6.227	15.27	15.96	15.608	1.972	31.30	
57	1.0391	17.1725	19.1275	18.188	.312	29.43	
58	1.0391	18.30	19.45	18.863	.3065	28.91	
59	1.024	14.1675	14.8950	14.524	.311	29.76	
60	1.024	14.845	15.485	15.158	.307	29.38	
61	1.024	14.31	15.6275	14.959	.301	28.81	

TABLE V.



No. of Exp.	$T_a$	$T_b$	$T_m$	$T_c$	$H = T_c \times \frac{1008.5 \times 948.24}{5}$	Mean $H$
	°	°	°	°	Cal.	Cal.
62	18.76	19.83	19.287	.1505	28.82	29.26
63	19.01	20.07	19.532	.148	28.34	
64	19.13	19.77	19.443	.157	30.06	
65	19.54	19.9075	19.718	.152	29.10	
66	19.9925	20.22	20.101	.1565	29.96	

TABLE VI.—ANALYSES.



Exp.	$x$	Grm. $\text{Al}_2\text{O}_3$ found in 50c.c. of Filtrate.	Grm. $\text{SO}_3$ found in 50c.c. of Filtrate.	$\text{Al}_2\text{O}_3$ in 100 pts. of Prec.	$\text{SO}_3$ in 100 pts. of Prec.	$\text{K}_2\text{O}$ in 100 pts. of Prec.	Per cent of total $\text{Al}_2\text{O}_3$ in Prec.
A	0.	.10766	.33231	0.	0.	0.	0.
B	1.5	.09788	.32651	63.93	36.07	....	9.55
C	2.0	.08310	.31883	64.56	35.44	....	22.81
D	2.5	.0689	.31134	64.89	35.11	....	36.00
E	4.0	.01995	.28588	65.39	34.61	....	81.47
H	4.79	.0	.28967	71.63	28.37	0.	100.
I	6.0	.0102	.32699	94.82	5.18	....	90.53
J	6.5	.0294	.32927	96.26	3.74	....	72.60
K	7.0	.0547	.33174	100.	0.	....	49.19
L	8.0	.1019	.33231	100.	0.	....	5.35



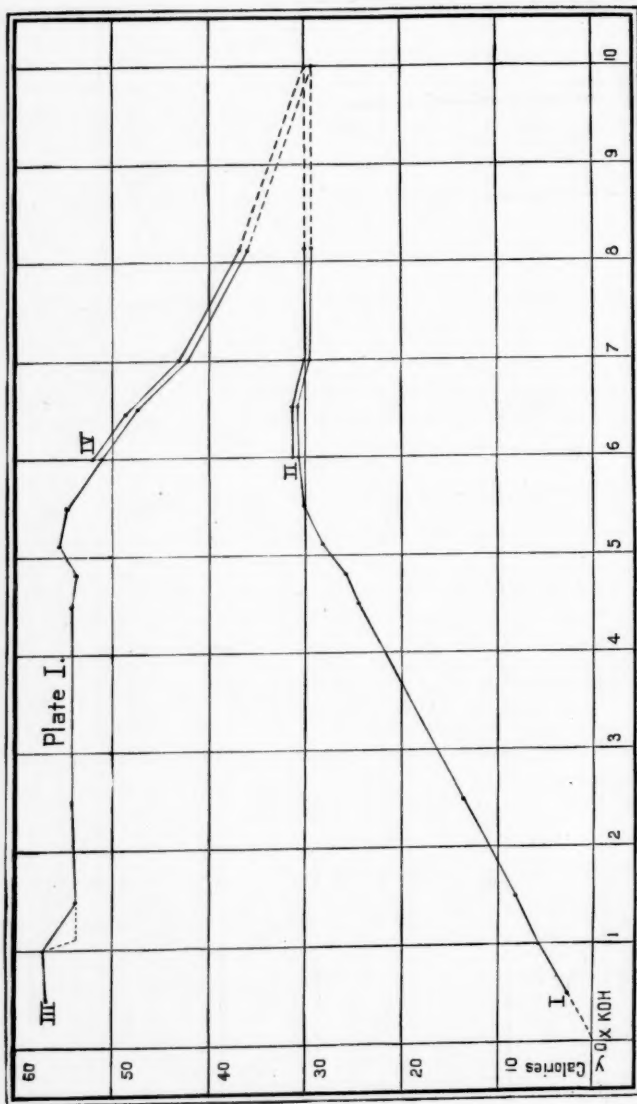


Plate II.

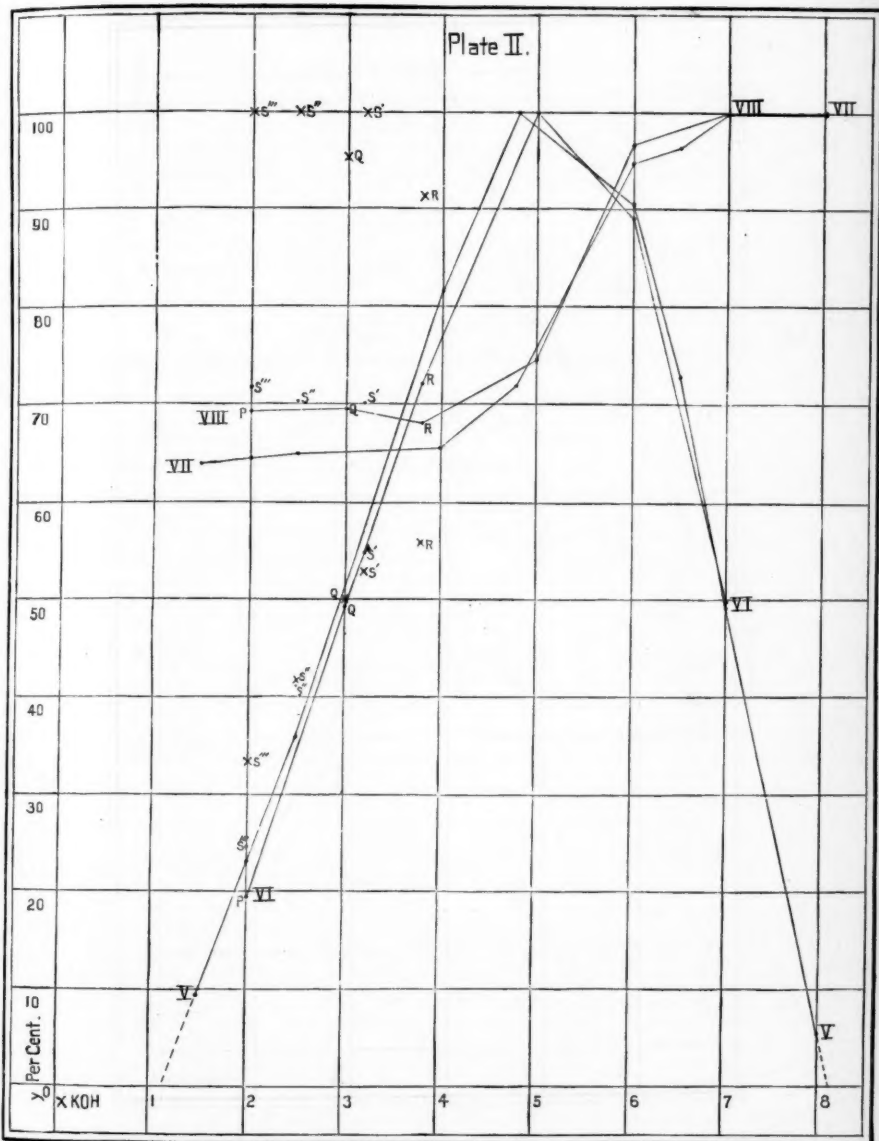




TABLE VII.—ANALYSES.

(1 Alum + 10 KOH) +  $x$  H<sub>2</sub>SO<sub>4</sub>.

Exp.	$x$ .	Grm. Al <sub>2</sub> O <sub>3</sub> found in 50c.c. of Filtrate.	Grm. SO <sub>3</sub> found in 50c.c. of Filtrate.	Al <sub>2</sub> O <sub>3</sub> in 100 pts. of Prec.	SO <sub>3</sub> in 100 pts. of Prec.	K <sub>2</sub> O in 100 pts. of Prec.	Percent of total Al <sub>2</sub> O <sub>3</sub> in Prec.
<i>N</i>	1.5	.0540	.45788 cal. .45679 found.	100.	0.	....	49.84
<i>O</i>	2.0	.0119	.50011 cal. .49673 found.	96.59	3.41	....	88.95
<i>T</i>	2.5	.0	.33231 cal. .29512 found.	74.33	25.67	0.	100.
<i>P</i>	4.0	.0867	.66969 cal. .66036 found.	69.20	30.80	....	19.47

TABLE VIII.—ANALYSES.

1 Alum +  $x$  KOH.

Exp.	$x$ .	Grm. Al <sub>2</sub> O <sub>3</sub> found in 50c.c. of Filtrate.	Grm. SO <sub>3</sub> found in 50c.c. of Filtrate.	Al <sub>2</sub> O <sub>3</sub> in 100 pts. of Prec.	SO <sub>3</sub> in 100 pts. of Prec.	K <sub>2</sub> O in 100 pts. of Prec.	Percent of total Al <sub>2</sub> O <sub>3</sub> in Prec.
<i>Q</i>	3.0	.0547	.30898	69.42	30.58	....	49.19
<i>R</i>	3.8	.0300	.29598	68.13	31.87	....	72.13
<i>S'</i>	3.2	.0516	.13951	70.11	29.89	....	54.78
<i>S''</i>	2.5	.0543	.15017	70.33	29.67	....	41.11
<i>S'''</i>	2.0	.0608	.15835	71.74	28.26	0.	24.57

## IX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.

## CRYSTALLOGRAPHIC NOTES.

By OLIVER W. HUNTINGTON.

Communicated by the Corresponding Secretary, June 10, 1885.

*Crystals of Azurite from Arizona.*

THE mineral cabinet of Harvard College has recently received, through the kindness of Mr. Godfrey Hyams, some very interesting groups of azurite crystals. The specimens came from the mines of the Detroit Copper Company, situated near Clifton in the extreme eastern portion of Arizona, and I am indebted to Mr. Hyams for the following description of their occurrence.

"The formation in which the deposits are situated is peculiar to these mines, so far as I know. The zones or belts of copper occur in a sort of felsite on a contact between lime and iron, the lime being calcite and the iron an oxidized compound of varying composition. Specimens analyzed have given results which show that hematite, limonite, turgite, and clay iron-stone all occur.

"The ore appears in different forms: —

"1. Malachite, as fibrous, botryoidal, stalactitic, encrusting, and massive.

"2. Azurite, fibrous, botryoidal, encrusting, massive, and lastly crystallized.

"The crystals occur in various ways; singly on or in different maniferous clays, in clusters like stilbite, in plates like nail-head spar, and in columns around a central axis like rock-candy.

"The two carbonates are in every phase of transition. We have malachite changing into azurite, that is, the malachite outside and azurite inside, then the reverse, malachite pseudomorph after azurite, and *vice versa*. Then again specimens of native copper occur in parts covered with crystals of cuprite, and these crystals in turn incrustated with malachite. With these are also large masses of cuprite,

chrysocolla, and some native copper, but as yet, even at a depth of over two hundred feet, no sulphides have been discovered,—a condition which is very unusual.

"There is another form in which the azurite is found, which resembles the Chessy deposits, that is, in a quartzose rock scattered in nuggets varying from the size of a pea to that of a walnut. All the ores carry, besides iron and silica, a small percentage of manganese and alumina, together with an amount of zinc varying from two to eight per cent."

The specimens received at the cabinet of Harvard College consisted of large masses of transparent crystals closely packed together, accompanied by beautiful stalactites consisting mainly of azurite, but coated over with malachite, the malachite usually covering the azurite.

Many of the crystals resemble closely those from Chessy, being grouped together so as to give a general rhombohedral aspect, having rounded faces and looking not unlike saddle-back crystals. These saddle-back crystals were all more or less rough, dull, and opaque; but with them were associated numerous brilliant transparent glassy crystals elongated on the ortho-diagonal, having the general aspect shown in the accompanying sketch (Fig. 1).

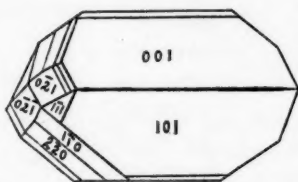


Fig. 1.

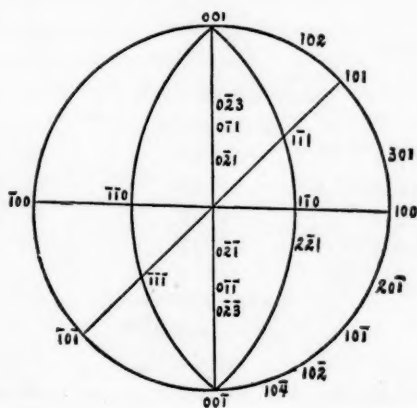


Fig. 2.

These crystals presented no new planes, and corresponded in their crystallographic elements so closely with those given by Des Cloizeaux that it seemed best to refer the planes to the same axial dimensions. The measurements were made with a reflecting goniometer, having a micrometer screw graduated to ten seconds; but since the planes were usually rounded or badly striated, the reading could only be accurately made in comparatively few cases, and in the table below the best angles have been indicated by heavy-faced type.

$$C = 87^{\circ} 39'. \quad c : b : a = 1.0378 : 1.1807 : 1.$$

## ORTHO-DIAGONAL ZONE.

## DES CLOIZEAUX.

001 $\wedge$ 102	27° 55'	26° 35'
001 $\wedge$ 101	47° 6'	<b>47° 3'</b>
001 $\wedge$ 301	74° 20'	<b>74° 20'</b>
001 $\wedge$ 100	92° 21'	92° 33'
100 $\wedge$ 20 $\bar{1}$	25° 16'	26° 8'
100 $\wedge$ 10 $\bar{1}$	42° 48'	43° 15'
100 $\wedge$ 10 $\bar{2}$	59° 44'	64° 28'
100 $\wedge$ 10 $\bar{4}$	73° 16'	70° 51'
00 $\bar{1}$ $\wedge$ 10 $\bar{4}$	14° 23'	17° 19'

## CLINO-DIAGONAL ZONE.

## DES CLOIZEAUX.

001 $\wedge$ 0 $\bar{2}$ 3	30° 21'	31° 31'
001 $\wedge$ 0 $\bar{1}$ 1	41° 17'	40° 22'
001 $\wedge$ 0 $\bar{2}$ 1	60° 21'	60° 37'
0 $\bar{2}$ 1 $\wedge$ 0 $\bar{2}$ 1	59° 18'	<b>59° 7'</b>

## PYRAMIDAL ZONE.

## DES CLOIZEAUX.

001 $\wedge$ 1 $\bar{1}$ 1	54° 40'	54° 44'
001 $\wedge$ 1 $\bar{1}$ 0	91° 48'	<b>91° 48'</b>
1 $\bar{1}$ 0 $\wedge$ 2 $\bar{2}$ 1	19° 58'	19° 46'
2 $\bar{2}$ 1 $\wedge$ 00 $\bar{1}$	68° 13'	68° 28'

## VERTICAL ZONE.

## DES CLOIZEAUX.

100 $\wedge$ 1 $\bar{1}$ 0	40° 14'	40° 16'
1 $\bar{1}$ 0 $\wedge$ 1 $\bar{1}$ 0	99° 32'	<b>99° 30'</b>
1 $\bar{1}$ 0 $\wedge$ 100	40° 14'	<b>40° 15'</b>

## OBLIQUE ZONE.

## DES CLOIZEAUX.

101 $\wedge$ 111	31° 53' 30''	31° 55'
111 $\wedge$ 111	116° 13'	116° 18'
111 $\wedge$ 101	31° 53' 30''	31° 50'

The planes of the main prism zone parallel to the ortho-diagonal, and those of the clino-diagonal zone, were very badly striated, and somewhat rounded, so that most of the measurements were made from mere flashes, only three of the angles being sharply defined. The remaining three zones were more sharply defined, and it will be noticed that in these zones the measurements more nearly coincide with those of Des Cloizeaux, and in every case they coincide within the probable limit of error due to the irregularity of the planes.

*Quartz Twins.*

In the September number of the American Journal of Science, Prof. W. G. Brown of the University of Virginia describes a group of twin crystals of amethystine quartz from Albemarle County, Virginia, which appear to resemble in structure twins originally described by G. Rose,\* and which he interpreted as twinned parallel to the fundamental rhombohedron, although united by a plane perpendicular to the same rhombohedral face. It appears, however, as originally shown by Nauman,† that the structure of these groups might be interpreted as twins of the ordinary type, parallel to a rhombohedral face, —  $\frac{1}{2}$  R, and the group examined by Professor Brown would seem to confirm this view, in so far as the corresponding rhombohedral faces of the twins are not absolutely in the same plane; although the irregularities he describes may obscure the small angular difference of twenty-six minutes, which could alone furnish decisive evidence as between the two theories under discussion.

Professor Brown also refers to the view of Ecle,‡ strengthened by the observations of Rath and Frenzel,§ and that of E. S. Dana,|| that

\* Poggendorf's Annalen, lxxxiii. 461, 1851.

† Elemente der Mineralogie, 6th ed., p. 190, 1864.

‡ Zeitschr. d. deutsch. geol. Gesellschaft, xviii. 428, 1866.

§ Poggendorf's Annalen, xvii. 155, 1875.

|| American Jour. of Science, III., xii. 448, 1876, and Zeitschr. für Krystall., i. 39, 1877.

similar twins might result from the growth of quartz crystals on a nucleus of calcite.

Through the kindness of Professor Brown the writer had an opportunity of measuring and studying the specimen from Albemarle County, Virginia, and he was thus led to measure with accuracy all the similar groups of quartz crystals in the mineral cabinet of Harvard College, and the following observations may be of value as additional evidence in regard to the phenomena in question. Out of a very large number of apparent twins, there were only three in which faces on any two individuals fell absolutely into the same zone, and in which an assumed plane of twinning could be referred, within the limits of error, to probable axial ratios.

The measurements on these crystals were as follows:—

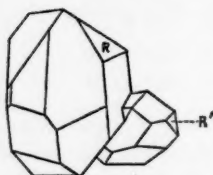


Fig. 3.

In the accompanying sketch (Fig. 3), we have  $R$  and  $R'$  in the same zone, and  $R \wedge R' = 21^\circ 32'$ . Axial divergence  $= 125^\circ 6'$ .

We find from this, that the assumed twinning plane would be a rhombohedral face with the axial ratio 0.4488, and this compared with the known fundamental ratio 1.0999 corresponds almost absolutely to a negative rhombohedron,  $-\frac{9}{22}$ .

With the group of crystals shown in Fig. 4 the same zone was measured, giving  $R \wedge R' = 50^\circ 26'$ . Axial divergence  $= 153^\circ 59'$ . Axial ratio for assumed plane of twinning  $= 0.19994$ . This compared with the fundamental ratio corresponds exactly to the negative rhombohedron  $-\frac{2}{11}$ .

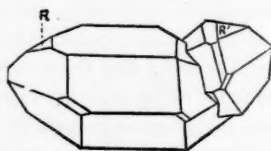


Fig. 4.

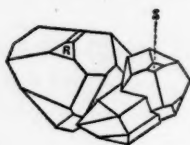


Fig. 5.

The group of crystals, Fig. 5, differed from the previous ones in having a plane of the direct hexagonal pyramid of one individual, and a plane of the indirect pyramid of the other, in a zone with the axes.

$R \wedge s = 14^\circ 44'$ . Axial divergence  $= 117^\circ 59'$ . Axial ratio of assumed plane of twinning  $= 0.3850$ . And this corresponds absolutely to the negative rhombohedron  $-\frac{7}{18}$ .

The examples here given show a wonderfully close coincidence with possible though somewhat complex ratios, but it must be re-

membered that these are only three out of a very large number of apparent twins, in which no such relation could be established. The following will serve as an illustration.

A group of crystals was found differing from the previous ones in no essential respects, in which  $R$  and  $R'$  were in a zone with the principal axes, making an angle with each other of  $4^{\circ} 8'$ . This would correspond to a twinning plane with an axial ratio of 0.63267, which bears no assignable relation to the fundamental rhombohedron. In other cases the approximation to possible ratios was much closer than this; but in most instances the planes on the two crystals were not even in the same zone, and every variation was noticed, from examples in which the reflected images would fall within the field of the telescope of the goniometer to those in which there was a much wider divergence, the crystals being displaced to a greater or less extent on the plane of twinning.

It will be seen by the above examples that in some cases the direct pyramid is in the same zone with the direct pyramid on the twin crystal, and in other cases it is in the same zone with the indirect; but intermediate positions were noticed, which would result from a greater or less rotation of one of the crystals on its own axis.

## X.

## TELESCOPIC SEARCH FOR THE TRANS-NEPTUNIAN PLANET.

BY DAVID P. TODD, M. A.

Communicated June 10, 1885.

IN the twentieth volume of the American Journal of Science, at page 225, I gave a preliminary account of my search, theoretic and practical, for the trans-Neptunian planet. I say *the* trans-Neptunian planet, because I regard the evidence of its existence as well founded, and further, because, since the time when I was engaged upon this search, nothing has in the least weakened my entire conviction as to its existence in about that part of the sky assigned; while, as is well known, the independent researches in cometary perturbations by Professor Forbes conducted him to a result identical with my own, — a coincidence not to be lightly set aside as pure accident.

That five years have elapsed since this coincidence was remarked, and the planet is still unfound, is not sufficient assurance to me that its existence is merely fanciful. In so far as I am informed, this spot of the sky has received very little scrutiny with telescopes competent to such a search; and most observers finding nothing would, I suspect, prefer not to announce their ineffective search.

The time has now come when this search can be profitably undertaken by any observer having the rare combination of time, enthusiasm, and the necessary appliances. Strongly marked developments in astronomical photography have been effected since this optical search was conducted; and the capacity of the modern dry-plate for the registry of the light of very faint stars makes the application of this method the shortest and surest way of detecting any such object. Nor is this purely an opinion of my own. But the required apparatus would be costly; and the instrument, together with the services of an astronomer and a photographer, would, for the time being, be necessarily devoted exclusively to the work. While, however, the photographic search might have to be ended with a negative result, in so far as the trans-Neptunian planet is concerned, there would still remain the series of

photographic maps of the region explored, and these would be of incalculable service in the astronomy of the future.

In the latter part of the paper alluded to above, I state the speculative basis upon which I restricted the stellar region to be examined; also the fact that between November of 1877 and March of 1878 I was engaged in a telescopic scrutiny of this region, employing the twenty-six inch refractor of the Naval Observatory. For the purposes contemplated, I had no hesitation in adopting the method of search whereby I expected to detect the planet by the contrast of its disc and light with the appearance of an average star of about the thirteenth magnitude. A power of six hundred diameters was often employed, but the field of view of this eyepiece was so restricted that a power of four hundred diameters had to be used most of the time. I say, too, that, "after the first few nights, I was surprised at the readiness with which my eye detected any variation from the average appearance of a star of a given faint magnitude: as a consequence whereof my observing-book contains a large stock of memoranda of suspected objects. My general plan with these was to observe with a sufficient degree of accuracy the position of all suspected objects. On the succeeding night of observation they were re-observed; and, at an interval of several weeks thereafter, the observation was again verified." Subjoined to the original observations are printed these verifications in heavy-faced type.

In conducting the search, the plans were several times varied in slight detail, — generally because experience with the work enabled me to make improvements in method. Usually I prepared every few days a new zone-chart of the region over which I was about to search; and these charts, while containing memoranda of all the instrumental data which could be prepared beforehand, were likewise so adjusted with reference to the opposition-time of the planet as to avoid, if possible, its stationary point. The same thing, too, was kept in mind in selecting the times of subsequent observation. Notwithstanding this precaution, however, it would be well if some observer who has a large telescope should now re-examine the positions of these objects.

Researches in faint nebulae and nebulous stars appearing likely to constitute a separate and interesting branch of the astronomy of the future, it has seemed to me that the astronomers engaged in this work may like to make a careful examination of some of the stars entered in my observing-book under the category of "suspected objects." The method I adopted of insuring re-observation of these objects was by the determination, not of their absolute, but only of their relative positions,

through the agency of the larger "finder" of the great telescope. This has an aperture of five inches, a power of thirty diameters, and a field of view of seventy-eight minutes of arc. Two diagrams were usually drawn in the book for each of these objects, — the one showing the relation of adjacent objects in the great telescope, and the other the configuration of the more conspicuous objects in the field of view of the finder. Adjacent to these "finder" diagrams are the settings, — to the nearest minute of arc in declination, and of time in right ascension, — as read from the large finding-circles, divided in black and white. The field of view of the finder is crossed by two pairs of hair-lines, making a square of about twelve minutes on a side by their intersection at the centre. The diagrams in all cases represent the objects as seen with an inverting eyepiece. As the adjustment of the finder was occasionally verified, as well as the readings of the large circles, there should be no trouble in identifying any of these objects, notwithstanding the fact that no estimates of absolute magnitude were recorded. The relative magnitudes, while intended to be only approximate, are still shown with sufficient accuracy for the purpose of the research, and the diagrams are, in general, faithful tracings from the original memoranda.

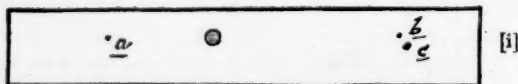
I transcribe the observing-book entire.

*Telescopic search for trans-Neptunian planet, with 26-inch equatorial.*

1877, Nov. 3.7. — Clamping polar axis, swept in declination, intending to detect planet by its supposed disk. Using power of 600, swept along plane of orbit, from long.  $155^{\circ}$  to  $166^{\circ}$ .

An object with slightly planetary look seen in  $\alpha 10^h 27^m$ ,  $\delta +10^{\circ} 0'$ .

An object (nebulous and about  $5''$  in diameter) found in  $\alpha 11^h 9^m.5$ ,  $\delta +5^{\circ} 28'$ :



It follows a star  $a 44^s.3$ ; and precedes  $b 69^s$ ;  $c 70^s$ .

Nov. 4.7. — Searching by same method,  $v$ ,  $148^{\circ}$  —  $163^{\circ}$ . Power 600. Soon clouded over.

Nov. 6.7. — Attempted method of survey by recording R. A.'s of stars in narrow zones, estimating  $\delta$  and magnitude which were recorded by Townsend. Success not satisfactory — chronograph gave trouble. Then went on with sweep in declination, using power 400.  $v = 163^{\circ}$

to  $168^\circ$ . Looked again for nebulous object seen Nov. 3.7. It has not moved. It is likely a nebulous star — a glistening point of light is seen from time to time in its centre.

Nov. 7.7. — Again tried method of search by recognition of disk. Improved by having dome all dark. I set with tangent screw in declination upon successive narrow zones, and sweep in R. A. Used power 600. Success good — shall try this method further. Clouded over between 16 and 17 hrs.

Nov. 11.7. — Swept carefully between  $9^\circ$  and  $10^\circ$  of my *plan* of to-day. Used power 600.

An object suspected,  $+9^\circ 45'$ .



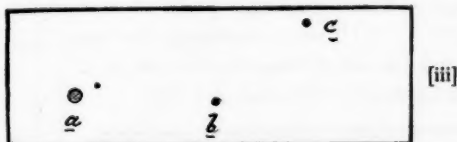
Object is *c*.  $ab = 24^\circ \pm$   
 $ac = 74^\circ \pm$

R. A.  $10^h 19^m \pm$

I do not much believe it to be anything but a star.

**Examined again, Nov. 13.7. Object a star.**

An object *a* about equally suspected,  $+9^\circ 35'$ , R. A.  $= 11^h 1^m$ . It has a faint companion,  $p = 96^\circ$ ,  $s = 25''$ .



$ab = 12^\circ.5$ . *c* is bright star and  $2' \pm$  south of parallel of *b*.

**Examined again, Nov. 13.7. Object a star.**

Twilight, however, prevented my seeing the comes.

Iris ⑦ Nov. 11.  $a = 3^h 43^m$ ,  $\delta = +24^\circ 50'$ .

After it began to be pretty light (about  $17^h.5$ ), I tried search by clamping in R. A., and sweeping in declination, following my adopted plane of the planet's orbit.

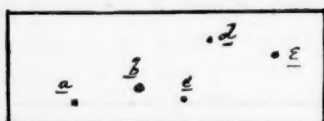
Set on  $\delta = +6^\circ.5$ .

$a = 11^h 12^m$ .

Suspected more fully an object which was too faint in the twilight to be compared with other stars near by. The instrumental position was,  $\alpha = 11^h 20^m.5$ ,  $\delta = +5^\circ 8'$ .

Tried power 890 on it, but did not get much of a disk. Look at this again.

Nov. 12.7. — Swept (not so satisfactorily as yesterday) between  $9^\circ$  and  $8^\circ 30'$ . Seeing not first rate. Used power 600. Faint nebula (probably) as follows, at  $b$ :



[iv]

$ab\ 9^s.7$ .  
 $bc\ 5.3$ .  
 $cd\ 2' \pm$ .  
 $de\ 2' \pm$ .

Instrumental position,  $\alpha\ 10^h 43^m.5$ ;  $\delta\ +8^\circ 58'$ .

$10^h 43^m$ .

$+8^\circ 50'$ .

5-inch finder, thus:

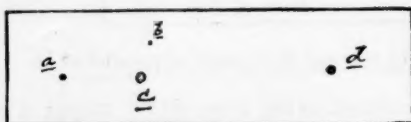


Examined again Nov. 13.7. Twilight prevented my seeing  $b$  and  $d$ . Look at this once more.

Examined again Dec. 2.7.  $b$  nebulous, but now plainly not round. Outline oblong, and jagged. It is a fixed object.

Nov. 13.7. — Good morning's work. Swept according to plan, from  $+8^\circ 30'$  to  $+7^\circ$ , only shortening the zones a little. An object which may be only a faint nebulous star at  $c$ .

Instrument  $\alpha = 10^h 48^m$ ;  $\delta = +8^\circ 30'$ .



[v]

$ac = 21^s$ .  
 $ad = 57^s$ .

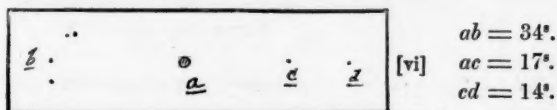
$b$  is faint companion to  $c$ , about  $2'$  distant, and  $p = 177^\circ$ .  $d$  is bright, and  $1'$  south of  $c$ .

Nov. 17.7. — Searched a short time for objects seen on the 12th and 13th. Was bothered variously, and search was ineffectual. Try again. Moonlight seems to interfere some. I think the object seen on the 13th is not now there.

Nov. 20.7. — Searched for object seen on the 12th. Either it is not now in the position then indicated, or (more likely) the full-moon

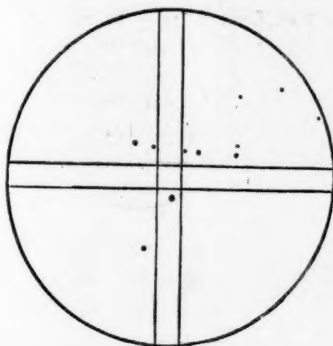
light prevents my seeing it. Try again, after the moon is out of the way — about Dec. 2.

Nov. 30.7. — Began search for object seen on 13th. Using power 600, swept carefully from  $+8^{\circ} 40'$  to  $+8^{\circ} 15'$  — zones about  $3'$  wide and  $20''$  long. Could find nothing at all nebulous, like what I saw on the 13th. No moon present. I then tried power of 400, and at about  $16^h.5$  hit on very faint object  $a$ . It is not at all like a faint star; but has a disk of nearly uniform illumination. So I compare it as follows, with one star preceding, and two following:



Instrumental position  $\left\{ \begin{array}{l} a \ 10^h \ 45^m \\ \delta \ +8^{\circ} \ 36' \end{array} \right\}$  painted circles.

The stars in the five-inch finder are these:



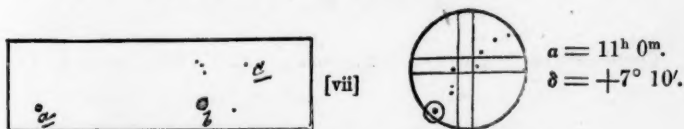
Some daylight at  $17^h.7$ , but could not then see  $a$ . Looked also for object seen on Nov. 12, but could not see it.

Dec. 2.7. — Settled all doubt about object seen on Nov. 12. Searched with power 400 for object seen on 13th, from  $+8^{\circ} 50'$  to  $+8^{\circ} 15'$ .

Zones  $20'' \pm$  long. Could find nothing. Either the object is not now there, or it is much less easily recognizable than I supposed

when I recorded so few stars near it. Shall now go on with the regular search.

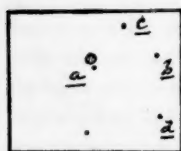
Dec. 3.7. — Object  $b$  not like star, though I cannot see a disk well.



$ab = 36''.5$ .  $a$  is north of  $b$  about  $1'$ .  $bc = 4'$ .

See Dec. 11.8. Also Dec. 12.7.

Object  $a$  suspected — it has a companion,  $p = 25^\circ$ .



[viii]

$$ab = 6''.7.$$

$$bd = 2''.5.$$



$$\alpha = 10^h 59^m.$$

$$\delta = +6^\circ 42'.$$

Swept with power 400, from  $7^\circ$  to  $6^\circ$  of plan of Nov. 11.

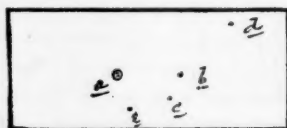
Dec. 11.8. — Objects  $a$  and companion are fixed.

Same Dec. 12.7.

Dec. 7.7. — Came over to observatory, but found dome disabled so that I could not go on with my work.

Dec. 9.7. — Began search from  $+6^\circ$ , south. Soon clouded up. Setting for next morning is  $+6^\circ$ , exactly. Began to look for objects seen Dec. 3.7; but clouds too dense to permit their being seen. Power 400.

Dec. 11.7. — Searched with power 400, from  $6^\circ$  to  $+4^\circ 10'$ . An object  $a$  suspected.



[ix]

$$ab = 8'' (10^h, \text{ s. t.}).$$

$$bc = 1''.5.$$

$$ce = 3'.$$

$$bd = 5'.$$

$$ab = 8''.4 (11^h, \text{ s. t.})$$



$$\alpha = 11^h 20^m.$$

$$\delta = +4^\circ 48'.$$

Dec. 14.7. —  $a$  is a very faint and small nebula. 1878, Feb. 11.7. — Did not succeed in seeing  $a$ .

Termination of search — a star in setting  $\alpha = 11^h 30^m$ ,  $\delta = +4^\circ 10'$ .

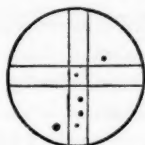
Finder.

Equatorial,  
Power 400.

Hunted up objects seen on Dec. 3.7. The first one has moved; or, at least, pointing as then indicated with the finder, I found objects in about the position of  $a$  and  $b$ , which I suppose to be the same—though daylight prevents saying certainly. These second objects are on the same parallel, and distant  $32^\circ \pm$ .  $c$  was also seen.

Dec. 12.7. — Examined objects seen on Dec. 3.7. The second one, fixed. The first one—I cannot decide whether it has moved since yesterday or not, as I had no opportunity then of observing it accurately. The setting for it is, better, this:—

$$\begin{aligned} a &= 11^h 0^m. \\ \delta &= +7^\circ 17'. \end{aligned}$$



5-in. finder.

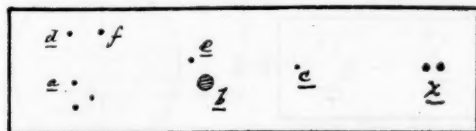
I now proceed to observe it accurately in R. A., and find by 14 chronographic transits that  $b$  follows  $a$  by  $31^\circ.92$ , at  $10^h.3$ , s. t.

$$b \text{ is south of } a \left\{ \begin{array}{l} 64.24 \\ 67.0 \\ \hline 22.76 = \text{''} \end{array} \right.$$

The object-glass is somewhat dewed; but I can see a companion to  $b$ , faintly—can only estimate:—  
 $s = 20'' \pm$ .  
 $p = 43^\circ \pm$ .

Dec. 14.7. — Mean of 3 chronograph transits,  $a$  precedes  $b$   $31^\circ.88$ . The companion to  $b$  is visible. I conclude that  $b$  is a fixed star: I have not at any time seen the trace of a disk on it. Curiously enough, there is a group of stars nearly south of this, about  $10'$ , which have nearly the same relative positions and magnitudes (except that  $a$  is much smaller). I think I must have observed this on Dec. 3.7 though I shall not now spend time to see. I believe also that  $ab$  is more than  $36^\circ.5$ , somewhat.

Go on with regular search—from  $+4^\circ 10'$  to  $+3^\circ 50'$ . (Object  $b$  large and nebulous.)



[x]



$$ab = 21^{\circ}.7.$$

$$bc = 5'.$$

$$ad = 3'.$$

$$be = 2' (p = 210^{\circ} \pm).$$

$$\alpha = 11^{\text{h}} 38^{\text{m}}.$$

$$\delta = +3^{\circ} 50'.$$

$x$  = object in centre of field of finder.

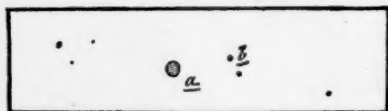
(Power 400.)

Search of this morning ends with this parallel.

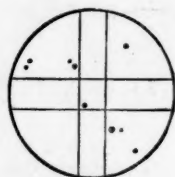
1878, Feb. 11.7. — Object  $b$  fixed. Instead of "large and nebulous," I should now record small, quite condensed, somewhat nebulous, and faint.

Dec. 19.8. — Bright light of moon, nearly full. Also some clouds passing. Attempted verification of object seen on 14.7. Saw the two stars  $x$ ; also  $d, f$ , and  $e$  without difficulty.  $a$ , and the two stars below it; also  $e$  and  $b$  were not visible.

Dec. 27.8. — Object  $b$ , seen on the 14th is fixed — probably a faint nebula. Going on with regular search, I suspect an object  $a$ : it has a small, but poorly defined disk.



[xi]



Power 400.

$$ab = 7^{\circ}.0 \text{ (from a few eye-and-ear transits).}$$

$$\alpha = 11^{\text{h}} 56^{\text{m}}.$$

$$\delta = +2^{\circ} 37'.$$

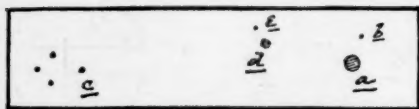
Finder.

1878, Feb. 6.6. — Object fixed.

Search of this morning ends with this parallel. Search not wholly satisfactory, as light of moon, one day past last quarter, interfered some. Still, think I missed nothing.

1878, Jan. 2.7. — Object  $a$  seen Dec. 27.8 is fixed. Farther south I find an object which is large and nebulous. Marked  $a$ .  $d$ , small, faint, and nebulous.

Finder.



[xii]



$\Delta a.$ 

$ab = 2^{\circ}.1 \ (15^h \ 55^m).$

$cb = 63^{\circ}.$

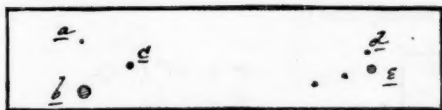
$ad = 23^{\circ}.1.$

$b$  and  $c$  should be nearly on the same parallel.

$\Delta \delta(ab) = 2'.5. \quad s(ed) = 1'.5.$

1878, Feb. 6.6. —  $d$  and  $a$  fixed.

Another pair of objects :



[xiii]



$b$  large and nebulous.  $e$  suspected somewhat.

$a$  precedes  $b \ 0^{\circ}.2.$

$b$  precedes  $c \ 5.7.$

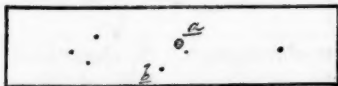
$d$  precedes  $e \ 1.4.$

All these objects are far from my adopted plane of orbit of trans-Neptunian planet.

1878, Feb. 6.6. —  $b$  and  $e$  fixed.

Jan. 5.7. — All four of the objects seen Jan. 2.7 are fixed. They are worth looking at again after two or three weeks, as they are near the present stationary point.

Another object,  $a$ , slightly suspected.



[xiv]



Definition so poor that it may be only a star blurred.

Finder.

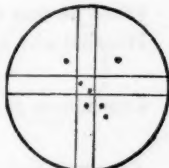


[xv]

$a = 12^h \ 5^m.$

$\delta = +2^{\circ} \ 0'.$

$a$  precedes  $b \ 5^{\circ}.5 \pm$   
(at  $5^d \ 17^h \ 40^m$ ).



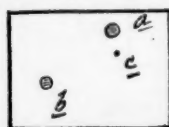
1878, Feb. 5.6. — Object fixed.

Object *a* has appearance of an elongated nebula. Beside the central condensation there is a minor and less marked one in the northern extremity (preceding).

Went on with regular search — that for this morning terminating with the above parallel,  $+2^{\circ} 0'$ .

Jan. 6.7. — At  $16^h$ , elongated object above precedes about  $5'.1$ , by eye-and-ear transits, roughly taken. Must observe it accurately on chronograph. The central condensation is not very sharp.

Object at bottom of preceding page [xiv] does not seem to be anything but a star with faint nebulous border. In fact, the one below it (and preceding), *b*, looks exactly like it.



[xvi]

$$ac = 45'' \text{ (est.)}$$

$$ab = 1'.7$$

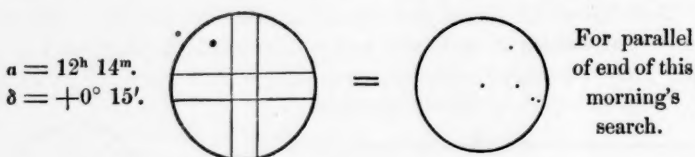
$$\angle acb = 96^{\circ}$$

$$p \text{ (c to b)} = 125^{\circ}$$

Look at this again, after a week or so.

#### 1878, Feb. 6.6. — Objects fixed.

Went on with regular search. Nothing suspected. Employed power 400. Search terminates with 4 mag. star in finder, thus : —



$$a = 12^h 14^m$$

$$\delta = +0^{\circ} 15'$$

Battery out of order — cannot use chronograph. So observed object at top of preceding page [xv] by eye and ear. Mean of several transits,

$$a \text{ precedes } b \ 5^s.04. \quad 13^h 30^m, \text{ s. t.}$$

Measured  $\Delta \delta$  with micrometer.

Fixed wire on *a*.

Movable wire on *b*, reads 55.62

'49

Coincidence 64.14.

55.56

64.14

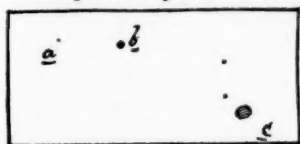
*a* south of *b* . . . . . 8'.58

$$= 85''.35.$$

Jan. 11.7. — Object (elongated and nebulous) observed Jan. 5 and 6 is still at same distance as on the 6th, so far as a few eye-and-ear transits would decide. The preceding and northern "condensation," observed on the 5th, now appears as a faint star, apparently shining through that wing of the slender, elongated "nebula."

Went on with regular search, power 400. Found curious configuration of stars — 12 and 13 mag. They form a nearly perfect square (about  $35''$  on a side). On same parallel as  $\eta$  Virginis, and following it about  $10^m$ .

*c* suspected object — faint and nebulous — outline quite regular.



[xvii]

$$\alpha = 12^h 18^m.$$

$$\delta = -0^\circ 20'.$$



Set rough circle at  $0^\circ$  so as to bring small triangle in centre of field of finder.

*a* precedes *b*  $8^s.2 \pm$ .

*b* precedes *c*  $13^s.6 \pm 0^s.07$  at  $17^h.5$ .

1878, Feb. 5.6. — Object fixed.

This morning's search terminates with this parallel.

Jan. 14.7. — Suspected object *c* (Jan. 11.7) fixed.

A nebulous cometary mass *a* (faint and irregular).



[xviii]

$$\alpha = 12^h 9^m.$$

$$\delta = -0^\circ 30'.$$



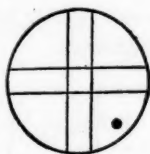
*a* precedes *b*  $4^s.1 \pm$ . Power 400.

1878, Feb. 6.6. — Object fixed.

Search ends ( $\gamma$  Virginis).

$$\alpha = 12^h 35^m.$$

$$\delta = -1^\circ 10'.$$



Elongated object first seen Jan. 5.7 is a nebula. I think it is Herschel (G. C. 2776).

Feb. 5.5. — Began search — finder thus: —

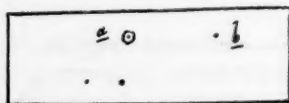
$$a = 10^h 9^m.$$

$$\delta = +13^\circ 30'.$$



Power 400.

Object *a* suspected.



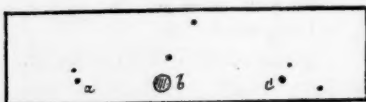
[xix]

$$a = 9^h 56^m.$$

$$\delta = +13^\circ 25'.$$



$$ab = 25.3 \pm 0.1.$$



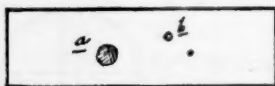
[xx]

*b* very faint and diffused.

$$ab = 32.5 \pm.$$

$$bc = 43.5 \pm.$$

Came upon an object — finder: —



[xxi]

$$a = 10^h 3^m.$$

$$\delta = +12^\circ 55'.$$



*b* pretty bright.

*a* quite faint, and seems to have a disk.

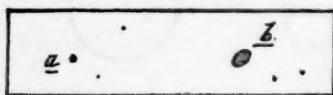
*a* precedes *b* (mean of 6 chronograph transits)  $28^s.17$  at s. t.  $11^h 12^m$ .

*a* precedes *b* (mean of 9 chronograph transits)  $28^s.35$  at s. t.  $14^h 6^m$ .

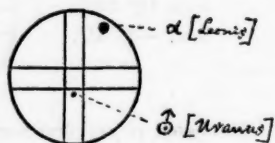
Feb. 6.5. — Object *a* (bottom of preceding page) [xxi] precedes *b*  $28^s.39$  (mean of 10 chronograph transits, at m. t.  $12^h 50^m \pm 10^m$ ).

Went on with regular search. Power 400.

Suspected object faint and diffused.

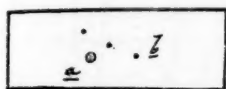


[xxii]



$$ba = 86^s.$$

Object *a* small and quite faint.



$$ab = 6^s.$$

[xxiii]

$$\alpha = 10^h 6^m.$$

$$\delta = +12^\circ 20'.$$



1878, Mar. 5.6. — Object fixed.

Continue search from this setting of finder — beginning with parallel of the wide pair.  $\delta = +12^\circ 8'$ .

Spent an hour or two in re-examining objects previously suspected. Notes accompany each object examined. Found all fixed — many small and faint nebulae.

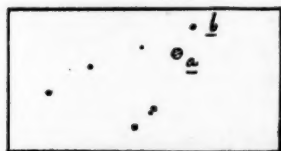
Feb. 11.6. — Object 10 lines above [xxiii], fixed — distance roughly  $6^s$ , by disappearance-transits.

Object *a* (bottom preceding page [xxi]) precedes *b*  $28^s.3$ ; (mean of two eye-and-ear transits). It still has the same appearance — very like that of a faint planet, with a small, ill-defined disk.

An hour or so in examining other objects previously suspected. Notes *loco*. Moon is beginning to interfere seriously.

Feb. 26.5. — Began search with power 400, at parallel  $+9^\circ 30'$ , going north.

Object *a* suspected — not a good disk — only regular and nebulous.



$$\Delta a.$$

$$ab = 3^s.25.$$

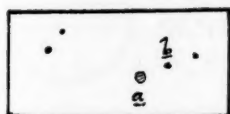
[xxiv]

$$\alpha = 10^h 31^m.$$

$$\delta = +9^\circ 35'.$$



1878, Feb. 28.5. — Object fixed.



$$ab = 1^s.5.$$

[xxv]

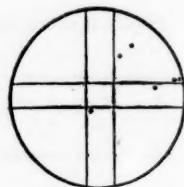
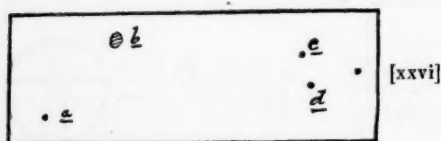
$$\alpha = 10^h 37^m.5.$$

$$\delta = +10^\circ 45'.$$



*a* very faint, and but faintly suspected.

1878, Feb. 28.5. — Object fixed.



$$ab = 7^{\circ}.9 \pm 0^{\circ}.1.$$

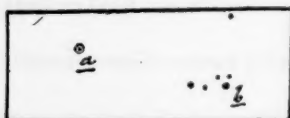
$$cd = 2^{\circ}.0.$$

$$\alpha = 10^{\text{h}} 30^{\text{m}}.$$

$$\delta = +10^{\circ} 55'.$$

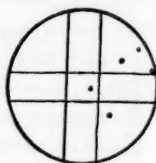
Morning's search terminates with this parallel.

Feb. 28.5. — Going on with search. Power 400. Verified places of objects seen Feb. 26.5.



$$\alpha = 10^{\text{h}} 15^{\text{m}}.$$

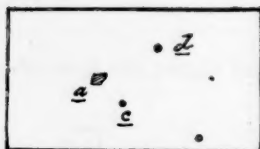
$$\delta = +11^{\circ} 0'.$$



$$\Delta a (ab) = 27^{\circ}.15.$$

*a* bright and very star-like — disk slightly suspected.

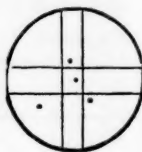
1878, Mar. 4.5. — Object fixed.



[xxviii]

$$\alpha = 10^{\text{h}} 30^{\text{m}}.$$

$$\delta = +11^{\circ} 10'.$$



*a* very faint — could not observe transits.

*ac* a little less than  $\frac{1}{2} ad$  or  $\frac{1}{2} cd$ .

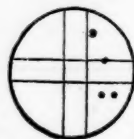
1878, Mar. 4.5. — Object fixed.



[xxix]

$$\alpha = 10^{\text{h}} 15^{\text{m}}.$$

$$\delta = +11^{\circ} 30'.$$



*a* quite faint; and nebulous (regularly).

$$\Delta a (ac) = (7^{\circ}.0) ??$$

1878, Mar. 4.5. — Object (probably) fixed.

Morning's search terminates with this parallel.

1878, Mar. 4.6,  $\Delta a(ac) = 5^{\circ}.2 \pm 0^{\circ}.1$ . I feel quite sure that  $a$  has not moved: the  $\Delta a(7^{\circ}.0)$  was put down from memory on March 2, without much hope of its being right. But, judging from the configuration, I say that  $a$  has not moved appreciably.

March 4.5. — Proceeded with regular search (power 400) after verifying objects seen Feb. 28.5+.



[xxx]

$$a = 10^h 26^m.5.$$

$$\delta = +11^{\circ} 50'.$$



$a$  like elongated nebula — rather faint. Centre of it about same R. A. as star  $b$ . I have represented it somewhat too far south — its centre should be nearer parallel of star  $c$ .

#### 1878, Mar. 5.5. — Object fixed.

Morning's search terminates with this parallel.

Put up instrument all in order at 1.45 A. M. Cahill, watchman — told him to wake me at 6 A. M.

March 5.5. — Proceeded with regular search (power 400), after verifying object seen yesterday.

Happened upon a nebulous mass — central condensation quite sharp — in  $a = 10^h 39^m$ ,  $\delta = +12^{\circ} 20'$ . I take it to be G. C. 2194, and so do not observe its position accurately: it is very bright.

Completed this morning the zone which fills up the gap to  $\delta = +12^{\circ} 20'$  (see Feb. 6.5); and went still farther north — to  $\delta = +12^{\circ} 40'$ .

So that the adopted plane of orbit of trans-Neptunian planet is now searched (without break) from

$$v = 146^{\circ}.8$$

to

$$v = 186.1.$$

Put up instrument all in order at 3 A. M., March 6, and went home at 3.45. Hayes, watchman in charge.

LAWRENCE OBSERVATORY, AMHERST, MASS.,  
7 October, 1885.

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INVESTIGATIONS ON LIGHT AND HEAT, MADE AND PUBLISHED WHOLLY OR IN PART WITH  
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## XI.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XXII.—COLORED MEDIA FOR THE PHOTOGRAPHIC  
DARK ROOM.

By WILLIAM H. PICKERING.

Communicated May 13, 1885.

SINCE the advent of the gelatine dry plate, many photographers have complained that their eyes are injured by the dark red light generally used in development. Considerable discussion of this subject has been aroused of late, but the only experiments made, as far as can be learned, have been to determine how much plates fog when exposed at the *same distance* to the various media tried. The experimenter then examines some object at that distance, and if he thinks he can see it about as well, and the plate is less fogged, the medium is pronounced an improvement.

In order to obtain more satisfactory results the following problem was proposed:—For a given distinctness of vision, what medium, or combination of media, will give the least fog on a gelatine plate? In order to determine at what distance from the lights equal distinctness of vision was obtained, a negative having some fine markings upon it was held at such a distance from the various sources that the details were just distinguishable from one another. Different portions of a sensitive plate were then exposed at these distances, one after another, to light coming through the different media, and the plate was then developed. Exposures with both daylight and gas-light as sources were made on the same plate, and, as was to be expected, those made by daylight were much the most fogged. If more colored glass was used, the daylight was too faint. So, for this reason alone, gas-light would be preferred. Add to this, that, if the gas-flame be placed at the bottom of a properly constructed flue, it will serve to ventilate as

well as light the dark room; and also that it can be used in the evening and on dark winter afternoons when daylight is out of the question. Moreover, since the gas-flame is much more uniform in brilliancy, it is correspondingly easier to determine when a plate is properly developed, and fewer plates are lost in this way.

Experiments with the following media have been made, and are numbered in the second and third columns in the order of their desirability. It will be noticed that there are five media which with gas-light give better results, i. e. less fog, than the best medium with daylight. In the second series the third column gives the distance in inches in each case at which the fine details were visible from the gas-flame. No medium is wholly satisfactory with daylight unless it contains red glass or paper. The window used with the gas-light measured six by seven inches, and was situated fourteen inches from the gas-flame. The window used with daylight measured five by five inches. Direct light from the clouds was used. The plate was developed in the first series with oxalate, and in the second with pyro and soda developer.

## FIRST SERIES.

Colored Media.	Gas.	Sky.
Red and yellow glass . . . . .	1	12
Red and ground glass . . . . .	2	6
Post-office paper . . . . .	3	14
Red glass . . . . .	4	8
Yellow glass double . . . . .	5	16
Yellow and violet glass . . . . .	7	18
Carbutt's red paper . . . . .	9	10
Red glass double . . . . .	11	13
Yellow and green glass . . . . .	15	17

## SECOND SERIES.

Colored Media.	Gas.	Inches.
Canary paper double . . . . .	1	8
Golden fabric double . . . . .	2	29
Red glass . . . . .	3	38
Golden fabric single . . . . .	4	58
Red, yellow, and ground glass . . . . .	5	11
Red and yellow glass . . . . .	6	22
Canary paper single . . . . .	7	19
Post-office paper . . . . .	8	15
Yellow and green glass . . . . .	9	41

It was found that ground glass transmitted fifty-five per cent of the light from a gas-flame coming through red glass, while it transmitted

only about nine per cent of daylight under similar circumstances. Its effect is therefore similar to yellow glass. The fact that the yellow-violet combination was so satisfactory with the gas-flame was probably due to the capacity of the yellow to cut off the small amount of violet emitted by this source, while it was quite inadequate to destroy it in the case of daylight, as is indicated by the figures. The precise order here given is not insisted on, but only the general sequence, as in the case of most of the media there was very little difference in their desirability, and sometimes the position of two media on the list would be reversed by a negative. One fact was brought out, however, with great distinctness in all the series, and that was the great inferiority of the yellow-green combination. This was of course to be expected, but, as many photographers still use this medium in their dark rooms, it was considered desirable to include it in the list, merely to show its inferiority. Although in the second series Canary paper double seemed to give the least fog of any of the media, the light transmitted by it proved to be so faint that it was quite inadequate for satisfactory illumination of the dark room; and, owing to its opacity, some doubt was cast on the accuracy of the observation. The second medium on the list has therefore been selected as the best practical one to employ with gas-light illumination. Its color is very pleasant to the eyes, and being translucent, instead of transparent, it lights the whole room in a very satisfactory manner. It is advisable to place it behind a sheet of glass, in order to protect it from being soiled by the chemicals employed. If one is obliged to use daylight as a source of light, it is probable that a sheet of red glass in connection with one or two thicknesses of Golden fabric would form as satisfactory a combination as any.

Experiments were next made to determine how bright a light is permissible with the medium adopted. The fish-tail burner which was used on the gas-lamp was placed fourteen inches behind a double sheet of Golden fabric, measuring twenty-four by sixteen inches. An extremely sensitive gelatine plate was placed at a distance of twelve inches in front of the medium, and a portion of it exposed for one minute. It was found, that if the gas-flame measured only one inch in height, not the least trace of fog was produced by the exposure. This is too faint a light for satisfactory use, however, and as a very minute amount of fog does not injure a negative perceptibly, and the direct exposure to the light in actual practice is much less than a minute, the flame is turned up to a height of an inch and a half or two inches for ordinary development. By this light one can readily see to

read the finest type, and the light pervading the whole room is very satisfactory. After a short exposure to it, in fact, it seems almost like white light.

In this connection may be mentioned a device which has proved very useful as an auxiliary in enabling one to judge of the proper development of a negative. A square hole measuring an inch and a half on a side is cut in the upper portion of the Golden fabric, and a piece of red glass inserted between the two thicknesses. If a negative be now held near this hole, a red square of light will be cast upon it. This square can be seen even when the lights of the negative are quite intense, and by noting its distinctness, one can judge of the opacity of the high lights as accurately as he can of the details of the shadows of the picture. If the high lights reach their proper intensity first, he develops for the shadows, and *vice versa*.

As the whole question of the proper medium to use resolves itself merely into what part of the spectrum to employ, red, orange, or orange-yellow, and all three of these yield nearly equally good results, it is evident that no important improvement can be made in the future. But as the orange-yellow is much the pleasantest light of the three, and seems to give rather less fog than either of the others, it is the color to be recommended. Any medium which will transmit this color will be found satisfactory, but Golden fabric is perhaps as convenient as any.

A very portable form of lantern to be used when travelling consists of a strip of Golden fabric a foot wide by two and a half in length. When one wishes to use it, it is rolled into a cylinder a foot long, and five inches in diameter, and pinned. A kerosene lamp with the wick turned down low, or a candle, is then placed inside, and the lantern is complete. The circle of white light formed on the ceiling is not bright enough to do any harm. The lantern is set several feet away from the exposed plates, and they should in general be protected as much as possible from direct illumination. There is then plenty of light, and yet not the slightest danger of fog.

## XII.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XXIII.—MEASUREMENT OF THE STRENGTH OF  
TELEPHONE CURRENTS.

BY CHARLES R. CROSS AND JAMES PAGE.

Communicated October 14, 1885.

So far as is known to the authors of the present paper, no measurements have ever been made of the strength of such telephone currents as are actually used in the transmission of speech. The few figures that have been given are estimates rather than measurements. Some very interesting results are given by Dr. C. J. Blake (*Jour. Soc. Tel. Engineers*, 1878, p. 247) regarding the logographic values of the different vowels as determined by the throw of the needle of a mirror galvanometer used in connection with a magneto transmitter. This logographic effect, however, should be carefully distinguished from that of the alternating currents utilized in the continuous transmission of sound, as, even with apparatus suitable for the measurement of such currents, it is liable to mask the phenomena to be studied unless care be taken to avoid such disturbing effects.

The lack of figures in so interesting and important a subject as the one under consideration arises from the fact that an electro-dynamometer of some form must be used for the necessary measurements, and an exceedingly sensitive instrument is essential in order to obtain sufficient deflection to give results of any value.

A form of electrical balance similar to that figured by Maxwell (*Electricity and Magnetism*, 2d ed., Vol. II. p. 342) was at first constructed, but this failed to give satisfactory results. Subsequently, success was obtained by using a Kohlrausch unifilar electro-dynamometer, made by Hartmann, of the form described in Wiedemann's *Annalen*, Vol. XV., 1882, p. 550. The instrument was modified by removing the heavy movable coil furnished by the maker, which was of altogether too low resistance for our purpose, and replacing it by a

lighter and closely wound coil of No. 36 (B. & S.) copper wire, with a suspending wire of the same gauge and 40 centimeters in length. The resistance of the instrument was 206 ohms, that of the suspended coil being 166 ohms. In some of the experiments the metallic vane, which in the instrument as described by Kohlrausch dips into a vessel of dilute sulphuric acid, was removed, and a needle point dipping into mercury substituted, the connection with the telephone being made through this. But the greater freedom from disturbances when the vane was used made it preferable. The rapid alternation of currents prevented any difficulty from polarization, as was shown by the fact that with a source of sound of constant intensity the same results were obtained whether dilute sulphuric acid or mercury was employed. A reading telescope and scale graduated to millimeters served to determine the deflections of the dynamometer coil, the telescope being at a distance of 1.5 meters from the mirror.

The dynamometer was usually placed in the secondary circuit of a small induction coil, the resistance of which was about 800 ohms. The microphone transmitters were placed in the primary circuit, with two Grenet cells arranged in parallel circuit. When the magneto transmitter was used it was placed directly in circuit with the electro-dynamometer.

The dynamometer was so placed that, when no current was flowing, the axis of its suspended coil was at right angles to the magnetic meridian. No special care was taken to secure this accurately, as the action of the deviating couple due to the earth's magnetism was found to be quite negligible in comparison with variations caused by unavoidable differences in the intensity of the sounds acting upon the transmitter. Deflections of the suspended coil were read by the use of a mirror, telescope, and scale, as the ordinary method of bringing the scale-reading back to zero by moving the torsion head of the instrument could not be used, since it was impossible with the voice to sustain a note for a sufficient length of time. The deflections were therefore read by the observer, and the strength of the current subsequently determined from these by the following method. A Daniell cell was placed in circuit with the dynamometer, using a mercury contact to avoid the polarization which would ensue with dilute sulphuric acid, and by means of a rheostat interposed in the circuit the resistance was varied until deflections were obtained corresponding with those given by the telephone currents. The electromotive force of the cell divided by the total resistance in the circuit gave the current corresponding to any given deflection. A galvanometer was also

inserted in the circuit; but as there was some uncertainty about its constant and law of deflection which we were prevented from determining by want of time, the method already stated was relied upon, merely using the figures given by the galvanometer as a check upon the results. The current strength as given in this paper is therefore the strength of the steady current which gives the same dynamometer reading as the alternating currents of the telephone. No correction for the self-induction of the dynamometer was attempted, as the range of variation in the readings shows that at the present stage of our research no real increase in accuracy would be secured by doing this.

The absence of any means of obtaining a definite and constant intensity of the voice renders it very difficult to obtain uniformity in results. Care was taken, however, not to continue the experiment very long at any one time, as the voice of the singer or speaker became wearied, and was less under control.

In telephonic experiments care must be taken, as already intimated, to avoid the logographic disturbance that arises from the strong air pressure developed on beginning the utterance of different sounds, as the magnitude of the temporary deviation produced by this often far exceeds the permanent deflection which is given by the continuous telephone current. This can be done by raising the voice very gradually; but a better method, which we have employed, is to interpose a key, which keeps the circuit open until the sound is fully developed. Then, on closing the circuit, the deflection quickly becomes steady, and the disturbance in question is avoided.

Measurements were made with the Hunning, Fitch, Blake, Edison, and Bell magneto transmitters. The Hunning transmitter uses carbon in a granulated form, and the Fitch employs two hard carbon disks as electrodes. The structure of the other transmitters is too well known to require any description.

The vowels *a*, *o*, *u*, *i* (German sounds) were spoken or sung into the transmitter successively, all at the same pitch, viz. the B of 480 vibrations, and with the same intensity as nearly as this could be realized. The deflections obtained are given below in full, in order to furnish some idea of the degree of uniformity obtained. Several separate series are given for each transmitter. In some cases the loudness of the voice varied somewhat in passing from one series to the next.

The readings are given in centimeters and tenths.

## HUNNING TRANSMITTER.

	<i>a.</i>	<i>o.</i>	<i>u.</i>	<i>i.</i>
(1.)	8.0	17.5	7.0	1.7
	7.5	12.2	7.0	1.3
	7.3	15.2	8.0	1.8
	9.2	12.3	8.4	1.8
	7.4	12.5	7.9	1.9
(2.)	11.5	15.5	9.8	4.0
	15.0	30.0	10.0	3.7
	15.0	20.5	11.0	3.5
	14.0	17.0	10.0	3.5
	12.5	18.5	11.0	3.0
(3.)	10.0	12.5	6.5	1.5
	10.0	11.5	7.5	2.0
	13.0	15.0	8.0	2.5
	11.5	12.5	5.0	2.5
	10.1	12.4	7.0	2.2
(4.)	12.5	13.0	8.0	2.0
	10.5	15.0	7.2	3.0
	12.5	15.0	9.0	2.5
	12.5	16.0	8.9	3.5
	12.0	16.0	8.7	3.5

## FITCH TRANSMITTER.

	<i>a.</i>	<i>o.</i>	<i>u.</i>	<i>i.</i>
(1.)	7.5	9.5	7.5	4.0
	5.5	9.0	7.0	4.0
	6.5	9.0	4.2	1.7
	5.0	6.5	7.0	4.5
	5.5	6.7	6.4	4.2
(2.)	6.2	8.0	5.7	1.8
	6.5	7.4	5.5	0.8
	5.0	7.4	5.4	3.8
	5.4	7.7	5.4	2.7
	6.4	7.0	6.0	2.0

	<i>a.</i>	<i>o.</i>	<i>u.</i>	<i>i.</i>
(3.)	6.0	7.4	6.1	2.1
	6.2	9.0	6.0	3.0
	6.4	8.2	5.5	2.7
	5.4	8.0	5.5	2.4
	5.7	8.0	6.2	3.2

## BLAKE TRANSMITTER.

	<i>a.</i>	<i>o.</i>	<i>u.</i>	<i>i.</i>
(1.)	0.5	0.3	0.2	0.0
	0.4	0.7	1.3	0.1
	0.4	0.8	0.4	0.0
	0.3	0.7	0.4	0.0
	0.4	0.7	0.3	0.0
(2.)	0.3	0.7	0.3	
	0.6	0.7	0.4	
	0.6	1.2	0.3	
	0.4	1.0	0.5	
	0.5	0.8	0.5	
(3.)	0.5	0.8	0.4	
	0.6	0.8	0.3	
	0.5	0.9	0.3	
	0.5	0.6	0.6	
	0.7	0.8	0.7	

## EDISON TRANSMITTER.

	<i>a.</i>	<i>o.</i>	<i>u.</i>	<i>i.</i>
(1.)	0.3	0.4	0.8	0.2
	0.3	0.5	1.1	0.1
	0.3	0.7	0.8	0.1
	0.2	0.7	0.7	0.1
	0.3	0.5	0.7	0.3
(2.)	0.3	0.5	0.7	0.1
	0.2	0.7	0.8	0.1
	0.2	0.7	0.8	0.2
	0.2	0.6	0.4	0.1
	0.4	0.7	0.3	0.2

	<i>a.</i>	<i>o.</i>	<i>u.</i>	<i>i.</i>
(3.)	0.4	0.9	0.5	0.1
	0.2	0.7	0.5	0.1
	0.2	0.8	1.1	0.2
	0.3	0.7	1.2	0.2
	0.4	0.8	0.8	0.3

## MAGNETO TRANSMITTER.

	<i>a.</i>	<i>o.</i>	<i>u.</i>	<i>i.</i>
(1.)	0.4	1.2	0.8	0.1
	0.3	1.3	2.3	0.3
	0.6	4.0	3.6	0.3
	0.4	2.9	5.4	0.5
	0.3	2.0	3.4	0.2
(2.)	0.7	1.0	2.1	0.2
	0.4	1.2	2.0	0.3
	0.6	1.3	2.0	0.7
	0.6	2.2	3.2	0.7
	0.8	2.7	2.7	0.5
(3.)	0.6	3.1	2.2	0.4
	0.6	2.7	2.3	0.3
	0.5	2.2	1.9	0.3
	0.6	2.3	2.4	0.5
	0.7	2.5	2.2	0.2

Some experiments were also made upon a Dolbear electrostatic receiver in circuit with a Hunning transmitter and high resistance induction coil. The currents produced when speech was readily transmitted and reproduced by the Dolbear receiver were too slight to be measured by the dynamometer, although amply sufficient to reproduce speech in a magneto receiver interposed in the circuit.

At first sight some of the results given in the preceding tables are quite unexpected. Thus in some cases the magneto transmitter gives a current as great as the Blake carbon transmitter, or even greater, although as used in actual practice the latter is far louder. This probably comes from the fact that with the magneto transmitter the lips were habitually placed close to the mouthpiece of the instrument, so that, even if the same actual strength of voice were used, the effect on the diaphragm of the magneto would be greater than on the diaphragm of

the Blake transmitter. It was impossible to use the same loudness of voice with the lips close to the mouthpiece of the latter transmitter, as the scratching sound which always appears with a microphone too strongly excited became very marked. Therefore, while keeping the voice at the same intensity, we removed the mouth farther from the transmitter, until the scratching ceased. In fact, the difference in the size and shape of the mouthpieces of the different instruments and the position of the mouth in speaking, whether pressed against the mouthpiece or at a little distance from it, always affect both the absolute and relative strength of the vibrations of the diaphragm with different vowels, and hence of the resulting currents. A further interesting illustration of this will be seen by comparing the results with the Hunning and Edison transmitters.

In another series of experiments the sound of a  $C_4$  stopped organ-pipe giving 512 vibrations per second was substituted for the voice. Very great constancy in its intensity was secured by blowing it with a blast and using a very large bottle as a pressure regulator. Three tubes were inserted through the cork of the bottle. Through one of these the air from the blast entered the bottle; through a second it passed to the organ pipe; while the third tube was drawn to a small aperture at its extremity, which allowed a greater or less quantity of air to pass out, according as the pressure from the blast tended to increase or diminish. Observations were made at intervals for ten minutes. Only slight oscillations of the coil occurred during this time. The following are the mean readings with different transmitters:—

Hunning . . . . .	7.9
Fitch . . . . .	3.4
Blake . . . . .	0.7
Edison . . . . .	0.2
Magneto . . . . .	0.5

The strength of the current in amperes in the different experiments was as follows.

#### VOWEL SOUNDS.

##### *Hunning Transmitter (from Series 3).*

Vowel.	Mean Deflection.	Current.
<i>a</i> . . . . .	10.9 . . . . .	0.000737
<i>o</i> . . . . .	12.8 . . . . .	0.000787
<i>u</i> . . . . .	6.8 . . . . .	0.000503
<i>i</i> . . . . .	2.1 . . . . .	0.000213

*Fitch Transmitter (from Series 3).*

Vowel.	Mean Deflection.	Current.
<i>a</i> . . . . .	5.9 . . . . .	0.000450
<i>o</i> . . . . .	8.1 . . . . .	0.000548
<i>u</i> . . . . .	5.8 . . . . .	0.000442
<i>i</i> . . . . .	2.7 . . . . .	0.000264

*Blake Transmitter (from Series 3).*

<i>a</i> . . . . .	0.6 . . . . .	0.000123
<i>o</i> . . . . .	0.8 . . . . .	0.000144
<i>u</i> . . . . .	0.5 . . . . .	0.000114
<i>i</i> . . . . .	— . . . . .	—

*Edison Transmitter (from Series 1).*

<i>a</i> . . . . .	0.3 . . . . .	0.000088
<i>o</i> . . . . .	0.6 . . . . .	0.000123
<i>u</i> . . . . .	0.8 . . . . .	0.000144
<i>i</i> . . . . .	0.2 . . . . .	0.000072

*Magneto Transmitter (from Series 2).*

<i>a</i> . . . . .	0.6 . . . . .	0.000123
<i>o</i> . . . . .	2.6 . . . . .	0.000260
<i>u</i> . . . . .	2.2 . . . . .	0.000238
<i>i</i> . . . . .	0.4 . . . . .	0.000103

SOUND OF C<sub>4</sub> ORGAN-PIPE.

Transmitter.	Current.
Hunning . . . . .	0.000550
Fitch . . . . .	0.000361
Blake . . . . .	0.000132
Edison . . . . .	0.000072
Magneto . . . . .	0.000114

In the case of some of the very small deflections observed, the current was calculated on the assumption that the deflection varied as the square of the strength of the current.

A few preliminary experiments were made, using a method by which we hope to obtain further results. A Thomson quadrant electrometer was used with the telephone on the same plan as that originally suggested by Joubert for its use with dynamo machines giving

alternating currents. The needle and one pair of the quadrants were connected with one terminal of the telephone, and the other pair of quadrants with the remaining terminal. There was not sufficient time at our disposal to obtain any series of measurements by this method, but results were reached which give encouragement as to its availability. It is possible that this method may prove especially useful in the study of electrostatic telephones.

The results given in the preceding pages are to be regarded only as preliminary to a more extended series of measurements. But while they are yet necessarily somewhat meagre, they at least show, first, that an electro-dynamometer of a simple construction is sufficient, not merely to detect, but also to measure telephone currents; and, secondly, that the strength of these currents, especially when good carbon microphone transmitters are used, is far in excess of what has hitherto been supposed.

ROGERS LABORATORY OF PHYSICS.

## XIII.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XXIV.—EXPERIMENTS WITH THE THERMAL  
TELEPHONE.

BY CHARLES R. CROSS.

Communicated October 14, 1885.

IN the *Telegraphic Journal* for 1880, p. 204, Mr. William H. Preece describes some very interesting experiments with a new form of telephonic receiver, consisting of a fine stretched wire, one end of which is attached to the middle of a diaphragm and the other to an adjustable support. The wire is placed in circuit with a voltaic battery and a microphone. When the microphone is actuated by the voice, the electrical undulations thereby produced in the battery circuit cause corresponding variations in the temperature, and hence in the tension of the wire, and thus the diaphragm is set into vibration, so that speech is reproduced.

Mr. Preece used six "bichromate of potash" cells. He does not state the amount of the heating effect on the wire, but from what is said it is evident that the temperature of the wire was but slightly elevated.

The statement of results in the paper referred to is quite brief; and the experiments detailed below were undertaken in order to ascertain to what extent speech can be reproduced by such a receiver, both as to loudness and intensity; to study somewhat further the changes due to variation in the length and diameter of wire of different materials, under varying conditions of current strength; and, especially, to observe the effect of varying the temperature of the wire. Most of the experimental work has been carried on, under my direction, by Messrs. W. J. Hopkins and J. O. Ellinger, students in the Laboratory of the Institute.

We first sought to find under what conditions we could realize the maximum loudness of speech using platinum wire, which had given

the best results with Mr. Preece. For a transmitter we used a Hunning microphone, a form of transmitter in which granulated carbon is employed, the powder being loosely confined between two metallic plates. The battery used consisted of from one to twelve Grenet cells, the maximum current used being sufficient to raise the temperature of a platinum wire, .01 in. in diameter and about 10 inches long, to redness. In order to avoid excessive heating of the transmitter it was placed in derived circuit with the battery and receiver. In some experiments the diaphragm was made of firm cardboard and in others of sheet-iron.

One would naturally suppose that the longer the wire, the greater would be the variations in tension, and hence the greater the loudness of the resulting sound. If, however, the length of the wire is increased beyond a certain limit, the quality of the articulation appears to become very inferior, even though the loudness may be somewhat increased; and the wire tends to assume a free vibration of its own, producing a confusing after-tone.

The heaviest wire that we used was 0.0095 in. in diameter, as want of the requisite current at the time of the experiments prevented our increasing the diameter beyond this. With it a length of about six inches gave in general the maximum loudness, as Mr. Preece had previously observed.

Using a platinum wire .004 in. in diameter and from six to seven inches long, with sufficient current to raise its temperature to dull redness, very remarkable results were obtained. Not only could the most unfamiliar conversation be understood, but words spoken into the transmitter were heard and understood with the ear at a distance of from two to ten inches from the diaphragm of the receiver, the character and loudness of the sound being very similar to that obtained when a Hunning transmitter is used with an ordinary magneto receiver. Using a somewhat shorter wire at the same temperature gave a decidedly better quality of sound, but the loudness was very materially diminished. Lowering the temperature caused a rapid diminution in the loudness of the sound.

Almost as good results were obtained with German-silver wire, a material not mentioned by Mr. Preece; but with this the influence of temperature was far less marked than in the case of platinum. In fact, quite as good results both as to loudness and distinctness of articulation were obtained when the wire was simply warm to the touch as when it was hotter. In this respect German silver differs from any of the other materials that we used. With iron and copper but few experiments were tried, and the results were quite unsatisfactory.

It is difficult to give any numerical estimate of loudness and distinctness in such experiments as these. The following tables, however, besides furnishing a more precise idea of our results, will show the result reached in some attempt to form a numerical estimate of the relative intensity under different circumstances. The loudness of an ordinary magneto receiver when used with a magneto transmitter, spoken into with a moderately loud tone of voice, is called 10.

*German-Silver Wire, Diameter .007 in., just below Redness.*

Length.	Nature of Articulation.	Comparative Loudness.
10½ inches . . .	Faint, but distinct . . . . .	3
7½ " . . .	Clearer . . . . .	7
5 " . . .	Same as in last experiment. . .	8
3 " . . .	Poor and indistinct . . . . .	4

*Platinum Wire, Diameter .0095 in., at Red Heat.*

10½ inches . . .	No sound . . . . .	0
7½ " . . .	Very faint. . . . .	1
5 " . . .	Quite distinct speech. . . . .	4
3½ " . . .	No sound . . . . .	0

*Platinum Wire, Diameter .006 in., just below Redness.*

10½ inches . .	Distinct . . . . .	Fairly loud.
7½ " . .	No change in distinctness. .	Loud as magneto.
6½ " . .	" " " . .	Louder.
4½ " . .	" " " . .	Much fainter.
2½ " . .	Very indistinct . . . . .	Barely audible.

In the last experiment the wire was cool when the shorter length was used.

*Platinum Wire, Diameter .005 in., just below Redness.*

7 inches . .	Speech easily understood . .	Moderately loud.
5 " . .	Clearer. . . . .	" "
3 " . .	Fairly distinct . . . . .	Fainter.

*Platinum Wire, Diameter .004 in., just below Redness.*

10½ inches . .	Speech fairly distinct . .	Faint.
7½ " . .	Very distinct . . . . .	Much louder.
3½ " . .	Clear . . . . .	Less loud.
2½ " . .	" . . . . .	"
1½ " . .	No sound . . . . .	Inaudible.

*Platinum Wire, Diameter .002 in., just below Redness.*

5 inches . .	Fairly distinct . . . . .	5
3 " . .	Less distinct . . . . .	9
1½ " . .	No sound . . . . .	0

From these and other experiments, it appears that our best results were obtained with the wire of .006 in. and .004 in. in diameter, there being but little difference between them. The largest wire used (.0095 in. diameter) gave very poor results; and with the battery power used by us the finest wire employed (.002 in. diameter) was equally inefficient. Mr. Preece's best results were secured with platinum wire .001 in. in diameter. Also with the finer wire the most effective length was less than with the larger sizes. The most interesting point, however, developed in the course of our experiments is the effect of increasing the temperature, notably with platinum wire, in increasing the loudness of articulation of the thermal receiver. This will naturally be attributed to the greater expansibility of the wire at high temperatures. It is possible that with German silver the effect, good at moderate temperatures, is not bettered on heating the wire, because of a marked influence of temperature in diminishing its elasticity.

The question also suggested itself as to what effect, if any, would be produced if the microphone were placed in the primary circuit of an induction coil, and the wire receiver in the secondary circuit, so that the receiver would only be acted upon by the induced currents from the coil. Since the heating effect varies as the square of the current, with such an arrangement difference of sign in the current could not be perceived at the receiver, and therefore one would not expect to be able to distinguish articulate speech. We thought that, if any sound was produced, it would be interesting to study its quality as compared with the quality of the sound actuating the transmitter. Our results, however, were negative. A sound was produced on breaking the circuit, but no audible effect was observed on speaking or shouting into the transmitter. In these experiments German-silver wire was used, in the hope that even at ordinary temperatures it might prove sensitive. Independent heating by a current of hot air was tried, but without success.

An attempt was also made to use the thermal telephone as a transmitter. Sir William Thomson has shown, in his researches on the electro-dynamic qualities of metals (*Math. and Physical Papers*, Vol. II. p. 208), that the electrical resistance of wires is varied by their tension, and indeed it was in following out this idea that Professor Hughes was led to his invention of the microphone (*Telegraphic Journal*, May 15, 1878).

Slight as the variation in resistance must necessarily be with such a transmitter, we yet hoped that the exceeding sensitiveness of the magneto receiver would suffice to detect it. Our results, while not at all

striking, were sufficiently encouraging to lead us to hope for greater ultimate success. The thermal telephone, with a platinum wire  $4\frac{1}{2}$  in. long and 0.004 in. in diameter, and an iron diaphragm, was placed in circuit with a battery of 10 Grenet cells and an ordinary hand telephone receiver. The current was sufficient to heat the wire almost to redness. All the joints of the wire were soldered to prevent the possibility of microphonic action, which at first caused some annoyance, but which was readily recognizable by the scratching sound produced by it. With the joints thus soldered, and every precaution taken to avoid such microphonic disturbances, we succeeded in hearing and understanding at the receiver the word "Hallo!" and some brief familiar sentences. The sound was low, but distinct and clear, and in quality quite unlike the sound produced by microphonic action. There seems to be no doubt that electrical undulations were produced in the circuit by variations in the stress to which the heated wire was subjected. Similar results were obtained with a smaller number of cells, even down to one; but the sound was then exceedingly faint and scarcely audible. Speech was also transmitted by a thermal transmitter in which German-silver wire was substituted for the platinum. It may be that the more marked results on heating the wire to a higher temperature by the use of a stronger battery indicate that at such a temperature the electrical effect of changes in stress in varying the resistance of a wire is increased.

ROGERS LABORATORY OF PHYSICS.

## XIV.

## EARLY EXPERIMENTS IN TELEGRAPHING SOUND.

By EDWARD C. PICKERING.

Communicated May 26, 1885.

IN 1870, when Professor of Physics at the Massachusetts Institute of Technology, I wished to show to an audience the experiment of transmitting sound by electricity. The only means of doing this, of which I was then aware, was by the sound produced when a piece of soft iron is suddenly magnetized or demagnetized. The sound thus produced is extremely feeble, and I proposed to replace it by the following device. Loud sounds may be produced by the vibrations of a plate, and a strong vibratory force may be applied to such a plate by means of an electro-magnet. The first receiver consisted of a powerful electro-magnet attached to the bottom of a wooden box, whose cover was replaced by a tin plate, to the centre of which a soft iron armature was attached. The dimensions were such that the armature was near the magnet, but not in contact with it. The plate appears also to have been used without the armature. It is not certain but that this form of apparatus may have been tried first, and the armature added to increase the energy of the vibration, and consequently the loudness of the sound. A tin box was also employed, the bottom of which replaced the plate and armature, and the box served to reinforce the sound. The transmitter was composed of a sonometer, around the wire of which a short wire was wound, dipping into mercury. An electric current was passed through both wires, the mercury cup, and the magnet. When the principal wire of the sonometer was set in vibration by a violin bow, or otherwise, the current was broken at each vibration at the surface of the mercury. When the circuit was made, the magnet drew the plate down, and when it was broken, the elasticity of the plate drew it back. A loud sound was thus produced, whose pitch could be varied by changing the length or tension of the wire of the sonometer. On December 13, 1869, I gave the first of eighteen lectures on Sound, forming one of the

Lowell Free Courses given that year at the Institute of Technology. It is probable that this experiment was prepared for and shown in the lecture of this course which was delivered on January 5, 1870, and related to sympathetic vibrations.

On August 23, 1870, at the meeting of the American Association at Troy, Professor R. H. Van der Weyde, of New York, presented paper No. 141 to Section A, in the hall of the Troy Female Seminary, Professor John M. Ordway acting as chairman. This paper was entitled, "Further Improvements in the Method of transmitting, audibly, Musical Melodies by the Electric Telegraph Wire." In the discussion which followed the presentation of this paper, I described my experiment, and pointed out that my difficulty was mainly with the transmitter, Professor Van der Weyde's with the receiver; also that, if he could combine his transmitter with my receiver, I thought he might obtain valuable results. I have since been informed that he adopted this suggestion, and ascribes to it the use of the metallic diaphragm which he afterwards employed. The "Troy Press" of the following morning, August 24, 1870, contained the following report of my remarks. On account of its importance, I may be pardoned for giving it verbatim.

"Professor Pickering described a simple means he had employed for rendering these vibrations audible. It consisted of a simple electro-magnet placed close to the bottom of a large tin box, whose resonance rendered the sound very intense. His remarks were greeted with marked approbation. Another member said Professor Pickering's method was beautiful in the extreme, because it did away with the armature."

Professor Charles R. Cross, then Assistant Professor of Physics in the Institute of Technology, was invited to give a lecture on Sound to the pupils of the New England Conservatory of Music, in February, 1872. He desired to show the experiment of telegraphing sound. Accordingly, Professor Cross, Mr. Waldo O. Ross (who was present at the experiment in 1870 also), and I spent an evening at the Institute, and repeated the experiment of 1870 under more favorable conditions. The great difficulty in the early experiment was with the transmitter. A tuning-fork was accordingly substituted for the sonometer, which enabled the circuit to be broken with greater certainty and regularity. It was, however, open to the objection, that sounds of one pitch only could be transmitted. The details of this experiment are known with much greater certainty than those of the first experiment. The battery consisted of six small Grove cells. An "Albert Biscuit"

box, 20 centimeters long by 12 wide and 12 deep, was first used as a receiver. Afterwards, a large tin packing-box, 80 cm. long, 50 cm. wide, and 50 cm. deep, was substituted for it, and gave a very loud sound. Most of this apparatus is still preserved at the Institute of Technology, and was used in the legal examination quoted below. In the last part of December, 1873, and the first week of January, 1874, a number of other experiments were tried by Professor Cross, and another exhibition of the instrument was made by him on January 7, 1874, at the first lecture of his Lowell Free Course of that year. Several forks were tried, and the receiver transmitted the characteristic sound of each, but one only was used publicly. The sound persisted when the magnet touched the box, but was then feeble.

Most of the above facts were testified to by Professor Cross in a legal examination held on June 18, 1879. It was agreed that the same deposition should be used in the two cases, *Harmonic Telegraph Company et al. vs. The New England Telephone Company*, and *Harmonic Telegraph Company et al. vs. Charles Williams, Jr.* Present, Caus-ten Browne, Esq., of counsel for complainants, Chauncey Smith and J. J. Storrow, Esqs., of counsel for defendants, and W. P. Preble, Jr., Examiner. Professor Cross also testified as follows:—

“*Ans.* On the 10th of June, 1879, I tried a number of experiments with this receiver, which was set up in a manner similar to its arrangement in the exhibition already mentioned, it being in the office of Mr. J. J. Storrow, Union Building, State Street, Boston. It, together with a Blake transmitter, was connected in the primary circuit of a battery; the transmitter being placed in Room 42, Union Building, and connected with the receiver by wires stretching across the open court separating these two rooms, and about one hundred feet in length. A second circuit, containing two ordinary hand telephones, was stretched between the two rooms, so that any messages sent by the apparatus which I am describing could easily be verified.

“The magnet in these experiments was placed near to the outside of one end of the tin box, which rested upon its side, and when faint sounds were transmitted the head was placed inside the box, with the ear opposite the poles of the magnet, in order to detect the sounds. I first asked Mr. Watson, who was assisting me, to play a small mouth harmonica before the mouthpiece of the Blake transmitter. I was expecting to hear the sound given by that instrument, and so was somewhat surprised to hear loud and clear notes resembling those of a music-box. On inquiring of Mr. Watson what instrument he had been using, I was informed that he had been transmitting the sound produced

by a child's music-box which he happened to have there. Afterwards the mouth harmonica was substituted, and its characteristic notes clearly perceived. In both of these cases the characteristic pitch and quality of the tones in the musical instruments used could be heard at the distance of eighteen inches or more from the receiver. Mr. Watson was then asked to speak into the transmitter, and, while the ear was still at a distance of about fifteen inches from the receiver, a sound was heard which was recognized as articulation, although the words could not be distinguished at that distance. I then placed my ear close to that portion of the box which was opposite the poles of the magnet, and asked Mr. Watson to speak into the transmitter. I then without difficulty was able to hear a number of sentences, which were entirely unexpected to me.

*Int. 9.* Please state whether on this occasion you also tried to transmit articulate speech, using as a receiver a common hand Bell telephone connected upon the circuit, with the mouthpiece and ordinary diaphragms removed, and the instrument held against one end of the tin box, so that the box should take the place of the diaphragm. And if so, with what result?

*Ans.* I did. With it we succeeded in transmitting articulate speech from one station to the other with very great ease.

*Int. 10.* Will the Institute of Technology give or sell the defendants the receiving apparatus you constructed, to be filed as an exhibit in this case? and if not, will you please produce duplicates of said tin box and horseshoe electro-magnet, and a wooden box like the one used in your experiment?

*Ans.* These early experiments have so much interest attached to them, that it seems desirable to retain the original apparatus in the possession of the Department of Physics. I will produce duplicates."

Copies of the apparatus were also presented, in May, 1885, to the defendants in the suit in equity, American Bell Telephone Company et al. *vs.* The Western Pennsylvania Telegraph and Telephone Company et al., Circuit Court of the United States, Western District of Pennsylvania, on motion for preliminary injunction. At this time, also, it was shown that articulate speech could be transmitted by the apparatus, by attaching a mouthpiece to one prong of the tuning-fork and placing a piece of carbon in the mercury under the style. Affidavits were also produced from Mr. G. W. Blodgett and Mr. L. W. Wood, stating that I showed the apparatus described above to their class in 1872. An affidavit of Mr. A. D. Blodgett shows that it was also shown to his class by Professor Cross in 1874.

The following extract from a letter to Professor Bell may also be of interest, as showing that I advised him to increase the sound of his telephone by an instrument resembling the Blake transmitter, in 1877, or two years before the invention of that instrument. This letter was written during the night following Professor Bell's communication on the telephone to the American Academy, on May 4, 1877. The telephone then exhibited gave a very feeble sound, and, according to my letter-book, I wrote on "the problem of introducing more kinetic energy into your telephonic circuit,—in other words, on making a telephonic relay. An idea occurred to me which I hope may give the desired result, and I shall be very glad if you have the means of giving it a trial. The problem is to utilize a local current, so that in a given circuit it shall be proportional to the current induced by the magnets. Now this may be done by attaching to the plate of the receiving telephone A, a fine wire, dipping in water, and nearly touching a wire connected with a second telephone and battery. The resistance of this circuit will be mainly that of the water between B and C. Now, as A vibrates, the interval B C will alter, and with it the total resistance, and consequently the current. Moreover, a feeble exciting current may regulate a powerful local battery." A sketch of the apparatus showed that the current from the battery passed through the vibrating diaphragm of a receiving telephone, to which was attached a wire B, dipping in water, and nearly in contact with a second wire C. The variations of the current thus magnified were then passed through a second telephone. A modification of the apparatus was also described, by which the current could be reversed, like the primary current. Had this instrument been tried, a loud-sounding telephone might have been obtained earlier. A carbon button should have been substituted for the liquid resistance, as the varying resistance of carbon was then well known.

No secret was ever made of these experiments, which were described and exhibited publicly and privately whenever this was desired. A patent for the apparatus was not taken out, from a belief that a scientific man should place no restrictions upon his work which would tend to prevent the repetition of an experiment of scientific interest. A full description should have been published. This was at first delayed from the pressure of other work and lack of appreciation of the importance of the results. Afterwards I was unwilling to enter into a controversy, or to obstruct my friends, who were struggling to obtain proper recognition of the great results they had obtained in the same field. Now that some of them, at least, have been amply rewarded, a

full statement seems necessary as a contribution to the history of the telephone.

It will be seen from the above statement, that in 1870, several years before the telephones now in use were invented, a receiver was devised, constructed, and tried, which consisted of a flexible iron diaphragm, supported at the edges and replacing the armature of an electro-magnet. Musical sounds were telegraphed successfully, and the apparatus was described at a scientific meeting, as the newspaper report shows. In 1872 and later, the experiment was repeated under various conditions. In 1879 it was shown that it was capable of serving as a telephone, and of rendering articulate speech audible at a distance. It appears to differ in no way in principle from the receiver now used. On the other hand, it should be stated that all my experiments were made, or were intended to be made, with a discontinuous current, and, although the instrument is capable of showing the variations of a continuous current, I did not have this application in mind when I constructed it.

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## XV.

## ATMOSPHERIC REFRACTION.

BY EDWARD C. PICKERING.

Communicated May 26, 1885.

## PART I.

DURING the summer of 1876 several thousand observations of the altitudes of the White Mountains were made by the writer.\* The method of zenith distances was employed, the instrument used being the micrometer level. Great difference of opinion exists among geodetists regarding the value of the zenith distance of a distant object as a means of determining its height, on account of the uncertainty in the atmospheric refraction. A large number of measures of this quantity were accordingly made in subsequent years, to show to what extent the observations of 1876 were likely to be affected by this error. Four micrometer levels have been employed, which will be designated as A, B, C, and D.

The first of these, A, was shown to this Academy on January 11, 1876,† and was exhibited at the International Exposition of 1876 in Philadelphia. It consisted of a telescope conveniently mounted, carrying a level, and having in the eyepiece a spider-line micrometer.

Instrument B, which was that used in 1876, was made out of an architect's level. It consisted of a telescope having an aperture of 3 cm. and a focal length of 25 cm., with an erecting eyepiece magnifying eighteen diameters. A delicate spirit-level was attached directly to the telescope, which rested in two wyes, 19 cm. apart. One end of the bar carrying these wyes rested upon a bearing, and the other upon the pointed end of a micrometer screw. The bearing and the nut of the screw were carried upon a bar which rotated around a vertical axis. A horizontal circle divided into degrees was added, for

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\* Appalachia, I. 138.

† Proc. Amer. Acad., XI. 256.

convenience in identifying the objects observed. The pitch of the screw was about 0.1 cm., and its head was divided into hundredths. The value of one division in seconds of arc was found by placing the instrument upon the cube of the telescope of the Meridian Circle of the Harvard College Observatory. A series of readings was then taken, setting the screw in various positions, and inclining the cube until the bubble showed that the small telescope was horizontal. The position of the bubble was then read, and the inclination determined by the large circle of the Meridian Circle. The value of one division was thus found, on June 7, 1877, to be  $13''.95$ . As the instrument is used only for small altitudes, the angles are practically measured by an accurate tangent screw on a circle about 38 cm. in diameter.

Instrument C is larger than B, and the cross-hairs in the latter are replaced by a filar-micrometer. It therefore combines the advantages of A and B. Its telescope has an aperture of 4 cm., a focal length of 45 cm., and a magnifying power of sixteen diameters.

Instrument D closely resembles B. Light is secured by the use of an inverting eyepiece. The aperture of the telescope is 2.5 cm., its focal length 21 cm., and its magnifying power ten. The value of one division of the screw was found as described above, and gave the result  $13''.95$ , or the same as B.

An important improvement was devised by Mr. J. R. Edmands, and introduced in this instrument, in March, 1882. The level was attached to the bar carrying the wyes, instead of to the telescope. As the instrument was originally used, the observations were rendered differential, the quantity measured being the difference in apparent altitude of the various objects. The only quantity liable to vary in using the instrument is the angle between the true level line and the axis of the instrument when the bubble of the level is the centre. This angle may be divided into two parts: first, the collimation error due to the deviation of the axis from the line passing through the centre of the pivots by which the telescope is supported in its wyes; and, secondly, the level error, by which this last line deviates from the horizontal when the bubble is in the centre. Each of these constants may be determined by the device proposed by Mr. Edmands. The level is attached to the bar carrying the wyes, instead of to the telescope. If now the telescope is turned around its axis  $180^\circ$ , the mean of the readings in the two positions will eliminate the collimation. The value of this constant is equal to one half the difference in these readings. The level error is similarly eliminated or determined by turning the telescope end for end around a vertical axis. Rotating the telescope around a horizontal

axis perpendicular to its own axis, gives both constants together, without distinguishing between them. The direction of the three axes around which the telescope should be rotated to give the collimation, level, or both combined, may be remembered as the axis of the telescope, the vertical cross-hair, and the horizontal cross-hair, respectively. With this modification, the micrometer level compares favorably with the vertical circle as regards economy in time and expense, portability, and accuracy when small angles are to be measured.

Before this modification, the difficulty in determining the combined level and collimation error was avoided by observing the difference in height of a distant and near mountain which are nearly in line. These were commonly so selected as to be in the same field of view. It was therefore only necessary to observe the difference in altitude by the micrometer screw under various atmospheric conditions.

The first series of measurements were made on Mt. Wachusett, in Princeton, Mass., on June 22, 1877. Accompanied by Col. C. W. Folsom, I reached the summit at about noon. The observations were begun at once with instrument B, and were continued with short intermissions until nearly eight o'clock, when darkness interfered. The following morning was exceptionally clear, and observations were begun at a quarter after four, and continued until two in the afternoon, when we left the summit.

Mt. Monadnock, Cheshire Co., N. H., was visited, July 3, 1877, by Mr. J. R. Edmands, Professor C. E. Fay, and myself. We reached the summit at about three in the afternoon, and began observing with instrument B. The air was so hazy that the Sandwich range was barely visible, and Ascutney, the Southern Kearsarge, and Gunstock were the most distant points observed. The observations were abandoned at about five o'clock on account of the increasing haze. On July 15, 1877, Mr. Edmands and I visited Mt. Washington, in the White Mountains, where we remained until July 24. The almost continuous cloud and haze prevented much work, except on July 18, when a few preliminary observations were made with instrument C; and on July 21 and 22, when observations were obtained with D. Mt. Kearsarge, Merrimack Co., N. H., was occupied at the same time by Mr. J. B. Henck, Jr., with instrument A, in order that simultaneous observations might be obtained at the ends of the line from Mt. Washington to Kearsarge.

Observations were undertaken in August and September, 1877, at Jefferson Hill, N. H., by Mr. Henck, and at East Jefferson, by Mr. Edmands, with instruments B and D, respectively. Again long

periods of storm and haze prevented the accomplishment of satisfactory work.

Some observations were obtained by Mr. Edmands from Mt. Starr King, Coos Co., N. H., in October, 1878. In November and December of the same year, Mr. Edmands resided at Arlington Heights, Mass., for the purpose of obtaining similar observations.

Plans were also made for occupying simultaneously for a week Mts. Moosilauk, Kearsarge (S.), and Wachusett, which lie nearly in a straight line. Observations could thus be obtained at the ends and near the middle of a line nearly a hundred miles in length.

Much time was lost, owing to bad weather, when stations were occupied which were especially adapted to the determination of the atmospheric refraction. That a very distant point might be seen, lofty and comparatively inaccessible stations were required. Moreover, in order that observations might be made under the extremes of temperature and other atmospheric conditions, it was necessary that the work should extend over a considerable period of time. A series of measurements was accordingly undertaken at the Harvard College Observatory, where the absence of very distant points was compensated by the ease with which observations could be made at all times and seasons without materially interfering with other work. The observations were begun on January 3, 1882, and continued until January 26. During this series the temperature fell as low as  $-15^{\circ}$  F. The position of the level was then changed, as described on page 269. A second series extended from May 6 to August 7, 1882, and included observations in which the temperature was  $+91^{\circ}$  F. All the observations were made with instrument D, by Mr. Edmands and myself.

Only the observations made at Wachusett and at the Observatory will be considered in the present paper.

### I. WACHUSETT.

The micrometer level was mounted on the sill of the north window of room No. 19, in the second story of the hotel, on the summit of Wachusett. This point is approximately 15m. north, 3m. west, and 4m. above the United States Coast Survey bolt in the top of the mountain. The effect of the unsteadiness in the support is almost entirely eliminated by the differential character of the observation. The observations were made by directing the telescope towards the mountain to be observed, and turning the screw so that the level-tube was nearly horizontal. The position of the screw, of the two ends of

the bubble, and the time, were then recorded. The telescope was next directed alternately to the distant and near mountains, five times to each, and the screw readings recorded. The level was then again observed. These measures constituted one set. Sometimes a third mountain was also observed, and sometimes the level was omitted. Care was taken never to move the telescope horizontally during a set, and when several points were observed, they were always measured in the same order.

Table I. gives in the first column the Greenwich mean time, expressed in hours and tenths, the beginning of the day being taken at Greenwich noon. The second column gives a designation for the object pointed at; and the third gives the corresponding mean of the readings of the micrometer screw. L is used to denote that the telescope was level, and the reading in the third column is here corrected for the position of the bubble. The objects belonging to the same set are indicated by placing the time opposite the first only.

The various designations in the second column have the following meanings:—

B. Barrett Hill. Top of trees on hill nearly in line with Moosilauk and Kearsarge (S.). E. Mt. Equinox. G. Gunstock. Gp. Gap Mt. Gr. Greylock. J. Joe English Hill. K. Kearsarge (S.). The object observed was the base of the house, a short distance from the summit. This is apparently the house which has been destroyed, and not that now standing a few feet only from the summit. Ki. Killington Peak. L. Level, as stated above. M. Moosilauk. Mn. Monadnock. P. Passaconaway. Pi. Piscataquog, the hill nearly in line with Whiteface. W. Whiteface. 1. Summit of Kearsarge (S.). 2. Top of house on Kearsarge (S.). 3. Summit of a cloud-dome, presumably over Mt. Washington. 4. Northwestern of the Uncanoonucs. 5. Southeastern of the Uncanoonucs. 6. Cupola of Barnard House, Arlington Heights. 7. Roof of barn placed in right-hand part of field to determine inclination of wire. 8. Roof of barn in left-hand part of field. The two sets in which this object was observed showed that the inclination of the wire equals 0.6 division for  $1^{\circ}.1$ , or about  $8''$  per degree, including error in level.

TABLE I.—JOURNAL.

G. M. T.	Object.	Setting.	G. M. T.	Object.	Setting.
h.			h.		
4.8	L.	142.86	12.1	G.	249.78
"	Mn.	72.40	"	J.	254.40
4.9	L.	140.77	12.2	G.	255.08
"	L.	27.80	"	J.	259.94
5.0	L.	138.97	12.3	W.	50.38
"	K.	227.91	"	3.	68.2
5.9	L.	150.04	"	Pi.	66.95
"	Mn.	80.72	12.3	G.	251.46
6.0	L.	148.31	"	J.	256.04
"	K.	237.22	12.5	G.	52.78
6.1	L.	146.97	"	J.	57.54
"	G.	259.16	12.5	W.	57.22
"	J.	261.74	"	Pi.	72.06
6.2	L.	150.45	"	G.	51.42
"	Kl.	230.78	"	J.	55.04
"	Gp.	256.16	21.0	L.	158.44
6.3	Kl.	228.96	"	G.	62.42
"	Gp.	255.01	"	J.	69.30
6.4	G.	256.02	21.1	L.	159.03
"	J.	258.74	"	P.	63.76
7.1	G.	255.70	"	W.	62.28
"	J.	258.88	"	Pi.	81.42
7.2	G.	256.14	21.2	G.	61.84
"	J.	259.18	"	J.	68.58
7.2	K.	231.06	21.6	G.	60.94
"	B.	244.44	"	J.	67.58
7.3	K.	231.18	21.7	L.	158.03
"	B.	243.82	"	P.	262.54
10.1	L.	154.98	"	W.	260.72
"	Mn.	85.00	"	Pi.	279.88
10.2	L.	150.97	21.8	L.	157.92
"	K.	264.74	"	M.	256.14
"	B.	276.48	"	K.	265.50
10.3	L.	261.46	"	B.	279.08
"	2.	262.70	21.8	L.	157.71
"	K.	263.72	"	Mn.	87.90
"	B.	272.70	21.9	L.	159.24
10.4	G.	256.04	"	Mn.	88.34
"	J.	260.10	22.0	L.	157.91
10.4	K.	223.98	"	Kl.	225.34
"	B.	247.70	"	Gp.	256.06
10.8	G.	261.08	22.2	L.	158.97
"	J.	265.22	"	M.	257.57
10.8	G.	260.02	"	K.	264.94
"	J.	263.74	"	B.	278.02
11.6	G.	253.82	22.3	L.	158.30
"	J.	258.26	"	P.	262.36
11.7	K.	257.02	"	W.	260.52
"	B.	268.34	"	Pi.	279.88
11.8	W.	255.76	22.3	L.	157.34
"	Pi.	269.02	"	G.	260.96
11.9	G.	255.18	"	J.	267.84
"	J.	259.34	23.0	L.	151.68
12.1	G.	249.08	"	Gr.	192.38
"	J.	253.80	23.1	L.	154.86

TABLE I. — *Continued.*

G. M. T.	Object.	Setting.	G. M. T.	Object.	Setting.
h.			h.		
23.1	E.	175.70	4.2	Pi.	281.28
23.2	L.	157.55	4.3	L.	154.19
"	P.	261.88	"	G.	264.52
"	W.	259.76	"	J.	268.42
"	Pi.	278.74	4.4	L.	154.12
23.3	L.	158.24	"	G.	265.36
"	M.	259.57	"	J.	268.06
"	K.	265.13	4.5	L.	155.36
"	B.	278.46	"	M.	286.40
23.4	L.	156.76	4.6	L.	153.44
"	G.	261.52	"	J.	267.20
"	J.	267.20	"	4.	264.75
23.6	L.	157.27	"	5.	265.90
"	G.	262.54	4.8	L.	152.96
"	J.	268.08	"	G.	264.32
0.7	L.	156.97	"	J.	267.48
"	G.	265.22	4.9	L.	152.16
"	J.	269.22	"	G.	263.40
0.9	L.	157.87	"	J.	266.84
"	Mn.	86.96	5.4	L.	179.24
1.0	L.	157.92	"	6.	360.44
"	Mn.	87.16	5.6	L.	144.92
1.0	L.	156.92	"	G.	255.54
"	P.	269.12	"	J.	259.76
"	W.	266.08	6.2	L.	148.97
"	Pi.	281.24	"	G.	260.52
1.1	L.	156.29	"	J.	263.64
"	G.	265.14	6.2	L.	151.08
"	J.	268.74	"	Mn.	81.20
1.2	L.	155.81	6.3	L.	148.97
"	G.	265.74	"	K.	263.28
"	J.	269.62	"	B.	273.94
1.4	L.	155.45	6.4	L.	148.87
"	J.	269.04	"	P.	264.78
"	4.	266.49	"	W.	262.02
"	5.	267.23	"	Pi.	274.90
2.6	L.	153.88	6.4	L.	149.60
"	G.	264.22	"	Ki.	228.44
"	J.	267.98	"	Gp.	254.22
2.8	L.	153.35	6.5	L.	148.87
"	G.	263.81	"	G.	259.60
"	J.	266.78	"	J.	263.26
4.2	L.	155.34	6.6	7.	29.84
"	G.	265.44	"	8.	29.24
"	J.	268.80	"	L.	149.56
4.2	L.	155.18	"	G.	261.38
"	P.	269.26	"	J.	264.12
"	W.	267.64			

Besides the above settings, the altitudes and azimuths of about thirty mountains were taken on June 22 between 6<sup>h</sup>.4 and 7<sup>h</sup>.1, and of about forty more on June 23, between 1<sup>h</sup>.4 and 2<sup>h</sup>.6. The total number of pointings of the telescope was 816, and of level readings

262, although the entire stay upon the mountain little exceeded twenty-four hours.

The most complete series of measurements relates to the comparative altitudes of Gunstock and Joe English Hill. Table II. gives in successive columns, first, the Greenwich time in hours and tenths; secondly, the height of the barometer reduced to  $32^{\circ}$  F. by means of the reading of the attached thermometer; and, thirdly, the temperature of the outer air in Fahrenheit degrees. These quantities are taken from curves drawn to represent the observations which were made at intervals during the day. The fourth column gives the zenith distance of the sun in degrees uncorrected for refraction. The next column gives the apparent height of Gunstock above Joe English in seconds of arc, being the observed micrometric distance multiplied by  $13''.95$ , the value of one division in seconds. From the assumed heights of the two hills and the apparent difference in altitude, the coefficient of refraction has been computed by Mr. Edmands, and is given in the last column but one of the table. A smooth curve was constructed with these values, and the last column gives the residual found by subtracting the result given by the curve from that given by observation. Any error in the assumed heights of the three points would alter the coefficient of refraction by an amount constant throughout the table, but would not affect the amount of its variation.

Several important conclusions may be drawn from Table II. The angular interval between the two hills gradually increased, and with it the coefficient of refraction gradually diminished, during the first afternoon. The changes were small during the last half-hour, notwithstanding the cooling of the air in the upper regions of the atmosphere, and other important meteorological changes caused by sunset. The following morning the refraction was much less, increasing during the morning, and becoming somewhat irregular during the day. These changes are much greater than the errors of observation, as is shown by the accordance of successive sets, especially on the afternoon of June 22.

Table III. gives the comparison of the observations of Passaconaway, Whiteface, and Piscataquog. The first column gives the time, and the second the angular interval between the first and third of these mountains expressed in seconds of arc. The next column gives the corresponding coefficient of refraction, and the fourth gives the residual found by subtracting from this coefficient the corresponding ordinate of the smooth curve deduced from the observations given in Table II. The last three columns give the corresponding quantities for the line Whiteface and Piscataquog.

TABLE II.—GUNSTOCK AND JOE ENGLISH.

G. M. T.	Barom.	Therm. F.	Z. D.	G. — J.	Coef. Refrac.	O. — C.
h.	in.	°	°	"		
6.1	27.62	62	25	36	.0708	+.0001
6.4	27.62	62	28	38	.0707	+.0001
7.1	27.64	61	35	44	.0702	— .0001
7.2	27.64	61	36	42	.0704	+.0001
10.4	27.69	57	70	57	.0693	— .0003
10.8	27.71	56	75	58	.0693	— .0002
10.8	27.71	56	75	52	.0697	+.0003
11.6	27.73	54	83	62	.0690	— .0001
11.9	27.74	54	87	58	.0692	+.0002
12.1	27.74	54	89	66	.0688	— .0001
12.1	27.74	54	89	64	.0688	— .0001
12.2	27.74	54	90	68	.0685	— .0003
12.3	27.74	54	91	64	.0688	.0000
12.5	27.75	53	93	66	.0686	— .0001
12.5	27.75	53	93	63	.0689	+.0002
21.0	27.87	46	94	96	.0665	— .0001
21.2	27.87	47	92	94	.0667	+.0001
21.6	27.88	48	88	93	.0667	+.0001
22.3	27.90	50	80	96	.0665	— .0003
23.4	27.91	53	68	79	.0677	.0000
23.6	27.92	53	67	63	.0678	.0000
0.7	27.94	55	55	56	.0694	+.0001
1.1	27.94	56	50	50	.0698	+.0003
1.2	27.94	56	48	54	.0695	— .0001
2.6	27.95	57	34	52	.0696	— .0003
2.7	27.95	57	32	41	.0704	+.0004
4.2	27.93	59	19	47	.0700	— .0001
4.3	27.93	59	19	54	.0695	— .0006
4.4	27.93	59	19	38	.0707	+.0006
4.8	27.92	59	19	44	.0702	+.0001
4.9	27.92	59	19	48	.0700	— .0001
5.6	27.90	59	21	59	.0692	— .0009
6.2	27.89	60	26	44	.0703	+.0002
6.5	27.88	60	29	51	.0697	— .0004
6.6	27.88	60	30	38	.0707	+.0006

TABLE III.—PASSACONAWAY, WHITEFACE, AND PISCATAQUOG.

G. M. T.	P. — Pl.	Ref.	O. — C.	W. — Pl.	Ref.	O. — C.
h.	"			"		
11.6	198	....	....	224	.0670	— .0021
12.3	....	....	....	231	.0667	— .0021
12.5	....	....	....	207	.0677	— .0010
21.1	243	.0669	+.0003	267	.0652	— .0014
21.6	242	.0671	+.0005	267	.0652	— .0014
22.5	241	.0670	+.0002	270	.0651	— .0017
23.2	235	.0674	.0000	279	.0647	— .0027
1.0	169	.0700	+.0005	211	.0675	— .0020
4.2	168	.0701	.0000	190	.0684	— .0017
6.4	141	.0712	+.0010	180	.0688	— .0013

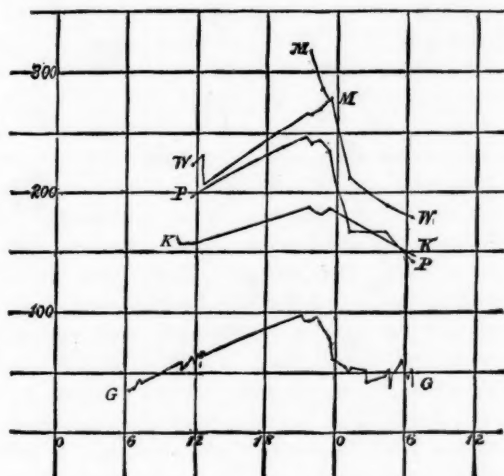
TABLE IV.—MOOSILAUKE, KEARSARGE, AND BARRETT HILL.

G. M. T.	M.—B.	Ref.	O.—C.	K.—B.
h.	"			"
10.2	....	....	....	164
10.3	....	....	....	167
11.7	....	....	....	168
21.6	319	.0697	+.0030	189
22.5	288	.0710	+.0043	182
23.3	278	.0713	+.0037	186
6.3	....	....	....	149

Table IV. gives the corresponding results for Moosilauk, Kearsarge, and Barrett Hill. The last two columns are omitted, since the height of Barrett Hill is not known with sufficient precision to compute them.

The height of the station occupied on Wachusett is 620 meters. The heights and distances of the various points considered in Tables II. and III. are as follows:—Gunstock, height, 730 m., distance, 121.5 km. Joe English Hill, height, 401 m., distance, 54.1 km. Passaconaway, height, 1280 m., distance, 167.5 km. Whiteface, height, 1221 m., distance, 164.7. Piscataquog, height, 368 m., distance, 48 km. Moosilauk, height, 1466 m., distance, 170.3 km. Kearsarge (S.), height, 897 m., distance, 99 km.

The general agreement of these results is shown in the following diagram, where abscissas represent times, and ordinates the angular distance given in Tables II., III., and IV. The letters G, K, P, W,



and M respectively indicate Gunstock, Kearsarge (S.), Passaconaway, Whiteface, and Moosilauk, as in Table I.

## II. HARVARD COLLEGE OBSERVATORY.

The station occupied was on the southern corner of the western balcony of the Sears Tower of the Harvard College Observatory. Its height is about 30 meters above mean tide level. Three points were selected very nearly in line which are designated below as *A*, *B*, and *C*. *A* is the summit of Fenno's Peak, the second highest of the Blue Hills of Milton, and nearly the most distant terrestrial object visible from the Observatory. Its height is about 160 m., and its distance assumed to be 18.865 km. *B* is the top of the chimney of the house No. 20 Terrace Avenue, Roxbury District, Boston. Its distance is assumed to be 7.042 km. *C* is the top of the roof at the base of the lightning-rod of the gasholder on Everett Place, Cambridge. Its assumed distance is 0.700 km. *B* is about 6' below *A*, and *C* about 17' below *B*. Each set consisted of nine settings in the order *A B C A B C A B C*, the readings being made to tenths of one division of the micrometer screw. The mean of the three readings of *A* was then subtracted from the corresponding means of *B* and *C*. The various sets are enumerated in Table V. The successive columns give a number for reference, the date, and the hour and tenth in Greenwich mean time. The day is here assumed to begin at Greenwich noon, or at about seven o'clock in the morning of Cambridge mean time. The only occasion on which the day changes during a series of observations is between Nos. 120 and 121. The barometric pressure in inches after correction for the temperature of the mercury, and the temperature in degrees Fahrenheit, are given in the next columns. These are followed by the intervals *AC* and *BC* expressed in seconds of arc. One division of the micrometer is assumed to be equal to  $14''.2$ , in accordance with a determination made at that time. As the observations are differential, the uncertainty in the value of this constant will be inappreciable in the result. The following column gives the zenith distance of the sun in degrees. The next two columns give the residuals in seconds, found by subtracting from the observed value of *AC* its mean value,  $1392''$ , and also the same residuals after applying the correction for temperature and pressure to be described below. The last column but one gives the probable error of a single setting, expressed in seconds of arc, derived from the accordance of the individual readings. The last column gives the initial of the observer. *E*. indicates the observations of Mr. Edmands, and *P*. my own observations.

TABLE V.—JOURNAL.

No.	G. M. T.		Bar.	Th.	A C.	B C.	Sun.	Res.	Res.	P. E.	Obs.
	1882.	h.	in.	°	"	"	°	"	"	"	
1	Jan. 3	3.5	30.01	+12	1406	1016	68	+14	— 5	3.3	P.
2	"	3.5	30.01	+12	1404	1008	68	+12	— 6	0.9	E.
3	"	8.3	29.98	+22	1404	1013	82	+12	— 9	3.2	P.
4	"	9.2	29.98	+20	1407	1014	88	+15	— 6	1.1	"
5	"	9.3	29.98	+20	1412	1016	89	+20	— 1	2.0	"
6	"	9.4	29.98	+19	1412	1013	90	+20	0	1.7	"
7	"	9.5	29.98	+19	1415	1010	91	+23	+ 3	1.7	"
8	"	9.6	29.98	+19	1420	1015	92	+28	+ 8	1.6	"
9	"	9.7	29.98	+18	1422	1016	93	+30	+10	2.3	"
10	"	9.8	29.98	+18	1423	1008	94	+31	+11	2.3	"
11	"	9.9	29.98	+17	1425	1020	95	+33	+14	5.3	"
12	"	10.0	29.98	+17	1450	....	96	+58	+39	7.5	"
13	Jan. 4	1.0	30.27	+ 3	1406	1002	77	+14	+ 1	3.3	"
14	"	2.0	30.30	+ 3	1405	1002	76	+13	0	1.8	E.
15	"	5.3	30.37	+ 6	1399	1006	67	+ 7	— 6	4.9	P.
16	"	6.1	30.39	+ 8	1404	1006	69	+12	— 2	3.0	"
17	Jan. 5	1.1	30.64	0	....	1040	82	....	....	4.0	"
18	"	5.2	30.68	+ 6	1423	1015	67	+31	+20	2.6	"
19	"	8.2	30.64	+20	....	1003	78	....	....	2.2	"
20	Jan. 7	0.9	29.85	+33	1405	1035	77	+13	—13	...	"
21	"	0.9	29.85	+33	1410	1007	83	+18	— 8	2.7	"
22	"	1.5	29.87	+34	1407	1008	78	+15	—11	2.1	"
23	"	2.7	29.89	+36	1401	1005	70	+ 9	+16	2.4	"
24	Jan. 22	3.2	29.45	+38	1403	1010	65	+11	+15	2.4	"
25	"	4.4	29.46	+38	1391	1000	62	— 1	+ 3	0.9	"
26	Jan. 23	3.6	30.01	+ 4	1398	1004	64	+ 6	— 9	2.2	E.
27	"	5.6	30.01	+ 5	1389	1000	64	— 3	+16	2.1	"
28	"	7.5	30.07	+ 4	1392	999	75	0	—14	1.8	"
29	"	9.2	30.11	+ 3	1394	1000	84	+ 2	—11	1.8	P.
30	"	9.6	30.13	+ 3	1398	1002	88	+ 6	— 7	5.2	E.
31	"	9.7	30.13	+ 3	1394	1003	89	+ 2	—11	2.0	P.
32	"	9.7	30.14	+ 2	1397	1008	89	+ 5	— 8	2.9	"
33	"	9.9	30.14	+ 2	1405	1006	91	+13	0	1.6	E.
34	"	10.0	30.15	+ 2	1395	1000	92	+ 3	—10	2.2	P.
35	"	10.1	30.15	+ 1	1414	1013	93	+22	— 3	2.0	E.
36	"	10.2	30.16	+ 1	1387	996	94	— 5	—18	4.9	P.
37	Jan. 24	0.4	30.59	—15	1407	1005	84	+15	+11	4.6	"
38	"	0.6	30.59	—14	1414	1010	82	+22	+17	0.9	"
39	"	1.0	30.59	—13	1410	1004	78	+18	+13	2.6	"
40	"	1.1	30.60	—13	1412	1013	77	+20	+15	2.7	E.
41	"	3.2	30.66	— 8	1409	1008	64	+17	+11	2.7	P.
42	"	6.3	30.64	+ 2	1389	999	66	— 3	—13	3.7	"
43	"	7.2	30.66	+ 3	1398	1004	72	+ 6	— 5	2.6	"
44	"	9.2	30.67	+ 4	1402	1009	84	+10	— 1	1.4	"
45	"	10.0	30.70	+ 3	1413	1018	92	+21	+10	3.3	"
46	Jan. 25	0.3	30.62	0	1430	1012	84	+38	+29	1.9	E.
47	"	0.6	30.62	+ 1	1440	1010	82	+48	+38	5.6	"
48	"	1.7	30.61	+ 4	1424	1001	73	+32	+21	1.9	P.
49	"	8.9	30.42	+26	1405	1000	81	+13	— 7	2.2	E.
50	"	9.9	30.41	+25	1405	997	91	+13	— 7	2.1	"
51	"	10.1	30.41	+25	1415	991	93	+23	+ 3	2.1	"
52	Jan. 26	7.5	29.79	+42	1411	1015	74	+19	—10	1.8	P.
53	May 4	1.7	29.71	+59	1386	1001	48	— 6	+ 6	2.4	"
54	"	2.9	29.70	+62	1382	994	36	—10	+ 1	0.9	"

TABLE V.—Continued.

No.	G. M. T.		Bar.	Th.	A C.	B C.	Sun.	Res.	Res.	P.E.	Obs.	
	1882.	h.	in.	o	"	"	o	"	"	"		
55	May	4	3.8	29.68	+65	1384	1002	29	— 8	+ 2	4.4	P.
56	"		5.0	29.65	+67	1383	996	27	— 9	0	9.3	"
57	"		5.2	29.65	+67	1397	1012	27	+ 5	+14	2.7	E.
58	"		5.8	29.62	+69	1378	991	29	—14	— 6	3.0	P.
59	"		8.0	29.57	+68	1369	982	49	—23	—14	7.4	"
60	"		8.6	29.58	+66	1383	996	54	— 9	0	2.2	"
61	May	5	0.8	29.78	+45	1386	995	57	— 6	+11	2.4	"
62	"		3.6	29.81	+47	1388	1005	31	— 4	+13	6.4	"
63	"		5.5	29.79	+48	1376	1000	28	—16	+ 1	5.8	"
64	"		8.7	29.77	+49	1370	988	56	—22	— 6	5.1	"
65	May	6	2.6	30.04	+47	1381	984	39	—11	+ 7	1.0	"
66	May	31	1.6	29.79	+66	1373	996	45	—19	— 9	5.8	"
67	"		1.7	29.79	+66	1381	991	44	—11	— 1	7.0	"
68	"		4.1	29.75	+74	1391	1008	22	— 1	+ 7	3.6	"
69	June	2	2.0	29.76	+53	1372	995	41	—20	— 7	2.2	"
70	"		3.4	29.78	+62	1384	1009	27	— 8	+ 5	2.2	"
71	"		4.7	29.79	+65	1379	1008	20	—13	— 2	1.0	"
72	"		10.6	29.77	+69	1373	995	72	—19	—10	1.8	"
73	"		12.4	29.79	+64	1418	1025	92	+26	+11	3.1	"
74	June	5	8.0	29.55	+68	1370	1000	44	—22	—14	3.0	"
75	"		9.0	29.55	+66	1382	994	55	—10	— 1	1.4	"
76	"		12.1	29.59	+63	1390	997	89	— 2	+10	3.0	"
77	"		12.4	29.60	+62	1409	1015	92	+17	+18	4.8	"
78	June	24	4.8	29.88	+86	1377	991	20	—15	—11	2.6	"
79	"		5.4	29.86	+88	1367	973	21	—25	+13	2.4	"
80	"		6.4	29.83	+90	1364	977	29	—28	+ 9	3.7	"
81	"		7.4	29.83	+91	1368	982	39	—24	+13	2.4	"
82	"		8.4	29.81	+91	1361	975	50	—31	+ 5	2.1	"
83	"		9.4	29.81	+91	1372	986	61	—20	+16	3.6	"
84	"		10.3	29.81	+89	1380	986	70	—12	— 9	3.3	"
85	July	11	7.2	29.62	+91	1369	987	37	—23	+12	2.1	"
86	"		9.1	29.61	+89	1385	991	58	— 7	— 5	3.1	"
87	"		9.4	29.60	+87	1384	993	61	— 8	— 6	1.6	"
88	Aug.	6	2.5	29.97	+80	1387	994	38	— 5	+ 1	1.9	E.
89	"		3.9	29.94	+86	1382	995	27	—10	— 5	1.8	"
90	"		5.7	29.93	+91	1386	994	29	— 6	— 3	2.8	P.
91	"		5.8	29.91	+91	1372	989	29	—20	0	3.1	E.
92	"		6.7	29.91	+91	1381	982	36	—11	— 8	3.4	P.
93	"		7.9	29.90	+88	1382	989	48	—10	— 6	1.4	"
94	"		8.7	29.89	+87	1384	983	57	— 8	— 4	2.2	"
95	"		9.7	29.88	+88	1378	988	71	—14	—10	3.1	"
96	"		10.7	29.88	+86	1389	999	79	— 3	+ 1	1.9	"
97	"		11.4	29.88	+84	1398	1005	85	+ 6	+11	3.1	E.
98	"		11.6	29.88	+84	1401	1012	87	+ 9	+14	1.3	"
99	"		11.6	29.88	+83	1396	1009	87	+ 4	+ 9	2.1	"
100	"		11.7	29.88	+83	1397	1005	88	+ 5	+10	3.0	"
101	"		11.9	29.88	+83	1402	1007	90	+10	+15	3.0	P.
102	"		12.0	29.88	+82	1395	998	91	+ 3	+ 8	3.2	"
103	"		12.2	29.88	+82	1395	995	93	+ 3	+ 8	1.4	"
104	"		12.3	29.88	+81	1390	990	94	— 2	+ 4	1.1	"
105	"		12.3	29.88	+81	1384	997	94	— 8	— 2	1.4	"
106	"		12.4	29.88	+80	1364	....	95	—28	+12	6.8	"
107	"		21.4	29.85	+71	....	997	98	....	....	0.3	E.
108	"		21.6	29.85	+71	....	995	91	....	....	1.5	"

TABLE V.—*Continued.*

No.	G. M. T.	Bar.	Th.	A C.	B C.	Sun.	Res.	Res.	P. E.	Obs.
	1882. h.	in.	o	"	"	o	"	"	"	
109	Aug. 6	21.7	29.85	+71	....	993	90	....	2.3	E.
110	"	21.8	29.85	+71	....	994	89	....	1.7	"
111	"	22.2	29.85	+71	....	1001	85	....	2.3	"
112	"	22.3	29.85	+71	....	1000	84	....	1.7	"
113	"	22.4	29.84	+71	....	998	83	....	2.8	"
114	"	22.4	29.84	+71	....	996	83	....	2.2	"
115	"	23.1	29.84	+71	1394	997	75	+ 2	2.8	"
116	"	23.2	29.78	+71	1396	1002	74	+ 4	2.3	"
117	"	23.4	29.79	+72	1395	999	72	+ 3	4.3	"
118	"	23.6	29.80	+72	1384	993	70	- 8	3.0	"
119	"	23.7	29.80	+73	1383	998	68	- 9	1.3	"
120	"	23.8	29.81	+73	1387	997	67	- 5	1.8	"
121	Aug. 7	0.0	29.81	+74	1389	997	65	- 3	2.1	"
122	"	0.1	29.82	+74	1404	994	64	+12	1.6	"
123	"	0.7	29.82	+76	1384	987	57	- 8	4.6	P.
124	"	1.7	29.80	+79	1387	987	47	- 5	3.1	"
125	"	2.7	29.80	+83	1384	988	37	- 8	3.9	"
126	"	3.7	29.80	+85	1382	985	29	-10	1.2	"
127	"	4.7	29.78	+88	1385	987	26	- 7	1.7	"
128	"	5.7	29.76	+88	1379	981	29	-13	1.9	"
129	"	6.7	29.73	+90	1362	975	37	-30	2.0	"
130	"	6.8	29.72	+90	1368	974	38	-24	1.6	"
131	"	7.4	29.72	+90	1365	974	44	-27	3.2	"
132	"	7.7	29.71	+89	1367	985	47	-25	2.3	"
133	"	9.5	29.70	+85	1392	1006	66	0	0.7	E.
134	"	9.6	29.69	+84	1384	1002	67	- 8	2.2	"
135	"	9.7	29.69	+84	1384	1003	68	- 8	1.4	"
136	"	9.9	29.69	+83	1385	1005	70	- 7	1.8	"
137	"	10.1	29.68	+83	1385	1005	73	- 7	2.3	"
138	"	10.3	29.68	+82	1381	1002	75	-11	2.1	"
139	"	10.4	29.68	+82	1392	1009	76	0	1.6	"
140	"	10.5	29.67	+81	1391	1003	77	- 1	1.9	"
141	"	11.6	29.67	+81	1395	1001	87	+ 3	1.6	P.
142	"	11.7	29.68	+80	1390	994	88	- 2	2.6	"
143	"	11.8	29.70	+80	1388	994	89	- 4	1.7	"
144	"	11.9	29.71	+79	1397	995	90	+ 5	1.6	"
145	"	12.0	29.71	+79	1393	991	91	+ 1	3.0	"

Additional evidence regarding the conditions under which these observations were made is furnished by the following notes.

1. Sun shining, snow on ground. Images somewhat unsteady.
12. *B* invisible, *A* and *C* difficult, owing to darkness.
15. Wind very high.
16. Image of *A* unsteady.
17. Hazy to south, but sun shining brightly.
20. The readings for *A* are 74.8, 79.7, and 98.8; for *B*, 03.6, 07.8, and 26.3; for *C*, 76.9, 81.2, and 98.2. The cause of this curious change is not certain. It was obvious to the eye, the cross-wires

appearing to withdraw from *A* after they had been set upon it. Ice had filled the holes in which the points of the tripod rested, and probably caused this motion. It may, however, have been due to a real change in the refraction, or to a change in the instrument, which had just been removed from a warmer place. In the subsequent sets the positions of *A*, *B*, and *C* remained constant near 91, 19, and 90.

24. Air unusually clear and steady. Wind high. Sun shining.

25. Cloudy.

26. Sun shining, wind high.

36. *C* difficult on account of darkness; settings discordant.

37. Air clear, wind light.

46. Hazy. *A* difficult.

53. Cloudy and a little hazy, but images good.

65. Images very bad.

74. Broken clouds, sun shining on *C* and Observatory.

75. Broken clouds, sun shining on *A*.

86. Heavy thunder-storm to the southwest.

87. *A* seen with difficulty owing to intervening rain.

107. *A* hidden in mist.

Fifty-two sets were taken during the winter, and gave the mean value of  $AC = 1408''$ , and  $BC = 1008''$ . The mean height of the barometer was 30.21 in., and of the thermometer  $11^\circ$ . Ninety-two sets were taken in warm weather, and gave  $AC = 1384''$ , and  $BC = 995''$ . Barometer 29.78 in., thermometer  $76^\circ$ .

The mean value of  $AC$  for the whole series was  $1392''$ , and that of  $BC = 1000''$ . The extreme range of the barometer was from 30.70 to 29.45 in., or 1.25 in. The thermometer varied from  $+91^\circ$  to  $-16^\circ$ , or  $107^\circ$ . The various values of  $AC$  differ from their mean of  $1392''$  on the average by  $16''.8$ . But nearly all of the residuals of the winter observations are positive, those in summer negative. If the residuals of each series are taken from the mean of that series, the average value is reduced to  $8''.5$ . This is nearly the same as  $8''.3$ , the mean of the residuals after correcting for temperature and pressure. The probable error of a single setting is  $2''.7$ , both in the winter and summer observations. Since three pointings are made on each object, the errors of observation are much less than the deviations due to refraction. Moreover, some observations are included in which one or more of the objects were seen with great difficulty, on account of haze, unsteadiness of the air, or increasing twilight. Probably the error due to phase caused by varying illu-

mination, personal equation, and other causes, greatly exceeds this, especially on an object like a hill-top, on which there is no signal to be observed.

To study the nature of the variations they have been grouped in Table VI., according to the zenith distance of the sun, the height of the barometer, the height of thermometer, and the logarithm of the correction for temperature and pressure according to Bessel's formula for refraction. In each portion of the table the first column gives the approximate mean value of the argument in each group; the second, the number of sets; the third, the mean value of *AC*.

TABLE VI. — GROUPING OF OBSERVATIONS.

SUN'S ZENITH DISTANCE.			BAROMETER.		
Z. D.	No.	<i>AC</i> .	Reading.	No.	<i>AC</i> .
°		"	in.		"
81	1	1405.0	29.40	1	1408.0
82	..	.....	29.50	2	1380.5
83	..	.....	29.60	10	1384.6
84	2	1398.0	29.70	22	1383.9
85	1	1398.0	29.80	30	1389.8
86	..	.....	29.90	20	1401.9
87	3	1397.3	30.00	16	1409.7
88	4	1398.0	30.10	6	1396.7
89	5	1396.2	30.20	3	1398.7
90	3	1403.7	30.30	2	1405.5
91	5	1402.6	30.40	5	1405.6
92	4	1409.2	30.50	..	.....
93	4	1411.5	30.60	8	1403.2
94	4	1396.0	30.70	5	1409.0
95	2	1394.5			
96	1	1450.0			

THERMOMETER.			BESSEL'S REFRACTIONS.		
Reading.	No.	<i>AC</i> .	Log.	No.	<i>AC</i> .
°		"			
-10	5	1410.4	-.030	35	1378.9
0	20	1403.5	-.020	30	1389.0
+10	5	1407.2	-.010	15	1386.3
+20	10	1411.9	.000	3	1377.3
+30	6	1408.2	+.010	6	1395.5
+40	4	1401.5	+.020	3	1407.3
+50	5	1380.2	+.030	13	1416.5
+60	8	1390.0	+.040	3	1399.7
+70	20	1384.8	+.050	15	1400.9
+80	28	1389.4	+.060	7	1413.7
+90	24	1374.5	+.070	5	1410.4

The first part of this table shows that no appreciable effect is produced on the refraction by the varying altitude of the sun. This conclusion was also derived from the observations on Wachusett. The group corresponding to a zenith distance of  $96^\circ$  consists of a single set, No. 12. The separate settings are discordant, the observation was very uncertain on account of the darkness, and *B* had become invisible. A variation in the refraction is obvious when either the barometer or thermometer varies. Low temperatures are, however, accompanied by high pressures, as is shown in the mean values given on page 282. The effect of these two causes cannot readily be distinguished. Probably both act, since both affect the density of the air. The grouping according to both temperature and pressure shows that this correction is a real one, and should be applied, although this is not customary in geodetic work.

TABLE VII. — CONSTANTS OF INSTRUMENT.

Date.	G. M. T.	Level.	Coll.	Alt.	Res.	Obj.
1882.	h.	"	"	"	"	
August 6	2.7	+19	+128	— 320	—3	<i>C</i>
"	3.4	+12	+126	— 322	—5	<i>C</i>
"	7.3	+29	+125	— 313	+4	<i>C</i>
"	11.4	+12	+133	+1083	...	<i>A</i>
"	"	+14	+129	+ 688	...	<i>B</i>
"	"	+14	+128	— 318	—1	<i>C'</i>
"	21.3	+ 1	+136	+ 681	...	<i>B</i>
"	"	0	+136	— 314	+3	<i>C'</i>
"	22.2	+ 2	+131	+ 687	...	<i>B</i>
"	"	+ 4	+131	— 311	+6	<i>C'</i>
"	23.2	+ 7	+132	+1078	...	<i>A</i>
"	"	+ 9	+132	+ 680	...	<i>B</i>
"	"	+ 7	+132	— 317	0	<i>C</i>
"	"	+ 8	+132	— 315	+2	<i>C'</i>
"	23.7	+11	+129	+1076	...	<i>A</i>
"	"	+ 6	+133	+ 680	...	<i>B</i>
"	"	+ 5	+133	— 315	+2	<i>C</i>
August 7	9.4	+ 9	+133	+1063	...	<i>A</i>
"	"	+ 7	+135	+ 680	...	<i>B</i>
"	"	+ 7	+135	— 323	—6	<i>C'</i>
"	10.1	+ 8	+129	+1068	...	<i>A</i>
"	"	+ 5	+130	+ 682	...	<i>B</i>
"	"	+ 3	+127	— 322	—5	<i>C'</i>

A series of measurements was made on August 6 and 7 to determine the steadiness of the constants of the instrument. In Table VII. the successive columns give the date, the Greenwich mean time, the level, the collimation, and the absolute altitude of the point observed,

in seconds of arc. The mean altitude of the nearer point,  $C$ , was found by these observations to be  $-317''$ , and the next column gives the residual from this mean. The last column gives the object observed,  $C'$  being employed to indicate a second point on  $C$ , which with certain illuminations was more readily seen.  $C''$  was found to be  $277''$  below  $C$ , and the measures of its altitude have been corrected by that amount.

The average value of the residuals in the last column but one is  $3.''4$ , which shows the degree of accuracy that may be attained with this instrument in determining absolute altitudes. The accuracy, portability, and cheapness of the micrometer level ought to render it useful for many purposes. Valuable work could be done with it from any station commanding a distant view. Observations of distant points in different azimuths, under varying meteorological conditions, are still much to be desired.

From the differential character of the observations described above, it has not been necessary to consider the curvature of the earth, or its variation in different azimuths, in the present discussion.

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INVESTIGATIONS ON LIGHT AND HEAT, MADE AND PUBLISHED WHOLLY OR IN PART WITH  
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## XVI.

## ATMOSPHERIC REFRACTION.

BY EDWARD C. PICKERING.

Communicated December 9, 1885.

## PART II.

THE observations described in Part I. relate exclusively to the refraction of the portion of the air between two objects on the surface of the earth. In astronomical observations we have to consider the effect of the entire column of air traversed by the light from an object outside the earth's atmosphere until it reaches the observer. The variation of this quantity, and the effect of local causes upon it, is an important source of error in many astronomical observations. For instance, the systematic differences in the declinations of the southern stars, as determined at different observatories, may be due to different refractions near the northern and southern horizons. The study of this matter has usually been left to the large alt-azimuths and transit-circles to be found in an astronomical observatory. From the fixed position of these instruments it is not easy to vary the conditions as much as might be desired. We are therefore ignorant of the variations of the refraction in different azimuths, or the effect upon it of the proximity of large masses of water, of forests, or of snow-covered mountains. Even its variations in different parts of the world are but little known, and it is usual to employ the refraction tables of Bessel, or those of the Pulkova Observatory, under the most varied conditions of climate or local surroundings. The micrometer level seems to be especially adapted to measuring the atmospheric refraction, and it is hoped that the observations described below will show that it is quite practicable for a traveller to determine this quantity at any point where the results are likely to be of interest. Not the least interesting of the results which may be thus obtained is the determination of the law regulating the refraction at great elevations.

The use of the micrometer level is limited to altitudes of three or four degrees; but within these limits the refraction and its uncertain variations are so large that angular measurements of great accuracy are not required. The only instruments needed are the micrometer level, a chronometer with some means of determining its error and rate, a barometer, and a thermometer.

The observations described below consisted in a series of determinations of the corresponding altitudes and times at which the sun or a star gradually approached the horizon. A complete observation consisted in observing the temperature and pressure of the air, and determining the error of the chronometer by comparing it with a standard clock whose error was known. The micrometer level was then placed in position on the west balcony of the dome of the Harvard College Observatory, and its collimation and level constants determined as described on page 269. The telescope was next turned nearly in the direction in which the sun or star would set, and several readings of the level taken in various azimuths. A series of measures was then made of the apparent altitude of the object as it approached the horizon, and the corresponding times. Finally, the preliminary measures, or such a portion of them as seemed to be essential, were repeated. When the sun was observed, the settings were first made on its lower limb until it disappeared below the horizon, and then the upper limb was measured until it also disappeared. For night observations, a fine needle was inserted in the field, and this formed a dark bar, which was visible against the sky without the necessity of a special field illumination.

A summary of the measures is contained in Table VIII., which gives, in successive columns, a number for reference, the date, the approximate Greenwich mean time, and the object observed. These are followed by the number of settings made, the corrected atmospheric pressure in inches, and the temperature in Fahrenheit degrees.

Series 2 to 8 inclusive were made by Mr. D. B. Pratt, the others by myself. Of the settings, 329 were made on *a Bootis*, 294 on the upper limb of the sun, and 122 on the lower limb, or 745 in all.

The value of the instrumental constants employed are given in Table IX. The successive columns give a number for reference, the date, and the Greenwich mean time. The next four columns give the apparent elevation of the object observed with the instrument placed in its four different positions,  $O_p$ ,  $O_v$ ,  $E_p$ , and  $E_v$ . The mean of these four readings gives the apparent height of the object. The excess of either of the four readings over the mean gives the correction to

TABLE VIII.—SUMMARY OF SERIES.

No.	Date.	G. M. T.	Object.	No. Obs.	Barometer.	Ex. Therm.
	1885.	h.			in.	°
1	Aug. 8	12.7	Sun	99	30.072	69.2
2	" 11	11.8	"	38	29.955	76.1
3	" 14	11.7	"	34	29.550	78.2
4	" 15	11.7	"	26	29.867	66.6
5	" 22	11.6	"	60	29.836	76.6
6	Sept. 2	11.2	"	76	30.034	55.0
7	" 2	15.3	$\alpha$ Bootis	39	30.034	55.0
8	" 3	11.2	Sun	83	30.012	59.9
9	" 20	14.2	$\alpha$ Bootis	51	30.222	48.0
10	" 21	14.1	"	45	29.991	52.1
11	Oct. 10	12.8	"	50	30.075	52.4
12	" 17	12.3	"	55	29.988	50.8
13	" 25	11.8	"	89	30.149	44.2

be applied to measures made in the corresponding position of the instrument. The position of the instrument actually employed was  $O_p$ , except in the observations to which Nos. 20 to 31 relate, when it was  $O_v$ . The corresponding excess is given in the next column. The last two columns give the values of the collimation and level error, in seconds of arc.

During September the level was used in some geodetic observations among the mountains of New Hampshire and Vermont. Nos. 20 to 25 were taken from the top of Mt. Moosilauk, and Nos. 26 to 31 from Mt. Mansfield. Although the instrument was carried in a wagon over rough mountain roads, the effect on its constants seemed to be inappreciable. The level error, as shown in the last column, did not appear to change perceptibly during the entire series. The collimation at first underwent a singular change which may have been due to a looseness of the screws holding the reticule. No change appears to have taken place during a single series of observations, since the collimation was always substantially the same before and after it, that is, in the pairs of measures made upon the same date. The effect is therefore eliminated in the final results. No change appears to have taken place after September 3.

Nos. 11, 15, 16, 19, 32, 33, 34, 35, 36, and 37 relate to the needle used to observe  $\alpha$  Bootis; in the other cases the intersection of the cross-wires was observed. The interval between them was about 85 divisions, which affects the collimation, but not the level, to this extent.

In No. 10 the reading of  $E_v$  has been assumed to be in error by one turn of the screw; otherwise, the observed value would be  $-46.7$ .

TABLE IX. — CONSTANTS OF INSTRUMENT.

No.	Date.	G.M.T.	<i>O<sub>p</sub></i> .	<i>O<sub>v</sub></i> .	<i>E<sub>p</sub></i> .	<i>E<sub>v</sub></i> .	<i>E<sub>x</sub></i> .	Col.	Level.
		h.						"	"
1	Aug. 8	11.6	— 16.1	— 21.7	+ 22.5	+ 15.1	+ 2.7	+ 45	0
2	" 8	12.7	— 17.1	— 18.8	+ 20.0	+ 15.7	+ 0.8	+ 21	0
3	" 11	11.5	— 18.0	— 19.0	+ 19.3	+ 17.0	+ 0.3	+ 11	— 3
4	" 11	11.8	— 18.0	— 19.6	+ 19.7	+ 18.0	+ 0.8	+ 11	0
5	" 14	11.4	— 21.0	— 13.4	+ 14.2	+ 22.1	— 3.3	— 54	+ 7
6	" 14	11.7	— 21.4	— 14.0	+ 13.0	+ 21.5	— 3.9	— 56	— 3
7	" 15	11.7	— 28.4	— 12.5	+ 8.6	+ 25.0	— 9.8	— 116	— 25
8	" 22	11.1	— 42.9	— 19.0	+ 19.7	+ 42.6	— 11.9	— 168	+ 1
9	" 22	11.6	— 41.9	— 19.2	+ 19.8	+ 42.8	— 11.0	— 160	+ 6
10	" 29	11.2	— 47.5	— 92.2	+ 93.1	+ 53.3	+ 24.0	+ 294	+ 24
11	" 31	11.4	— 21.5	— 161.2	+ 160.6	+ 23.0	+ 70.1	+ 967	+ 3
12	Sept. 1	11.0	— 35.5	— 10.0	+ 9.7	+ 33.4	— 13.3	— 172	— 9
13	" 2	10.8	— 36.0	— 10.7	+ 9.6	+ 33.8	— 13.5	— 173	— 11
14	" 2	11.2	— 36.7	— 7.2	+ 7.8	+ 36.4	— 14.7	— 193	+ 1
15	" 2	14.7	+ 123.0	— 17.4	+ 15.7	— 123.5	+ 69.6	+ 976	— 9
16	" 2	15.3	+ 123.0	— 17.2	+ 30.6	— 131.5	+ 71.3	+ 1054	+ 14
17	" 3	10.7	— 28.2	— 17.4	+ 16.5	+ 26.5	— 6.0	— 73	— 9
18	" 3	11.2	— 26.2	— 16.7	+ 17.2	+ 28.4	— 4.1	— 73	+ 10
19	" 3	16.1	+ 130.1	— 26.3	+ 27.0	— 122.0	+ 80.4	+ 1066	+ 31
20	" 6	3.6	— 148.3	— 149.3	+ 153.9	+ 150.1	+ 2.1	+ 17	+ 22
21	" 6	6.0	— 150.1	— 153.0	+ 154.5	+ 150.6	+ 1.9	+ 24	+ 7
22	" 7	1.6	+ 75.1	+ 70.7	— 70.6	— 74.8	+ 2.3	— 31	+ 1
23	" 7	4.8	— 176.5	— 180.5	+ 181.4	+ 177.9	+ 2.6	— 27	+ 9
24	" 7	7.9	— 177.4	— 180.5	+ 180.6	+ 177.5	+ 1.6	+ 22	0
25	" 7	11.8	— 112.8	— 116.2	+ 116.9	+ 112.0	+ 1.4	+ 29	0
26	" 10	4.0	— 215.9	— 211.4	+ 212.4	+ 216.3	— 1.9	+ 29	+ 6
27	" 10	6.6	— 177.9	— 181.6	+ 181.6	+ 178.3	+ 1.9	— 25	+ 1
28	" 12	8.0	+ 79.0	+ 74.3	— 73.2	— 79.8	+ 2.4	+ 39	+ 1
29	" 12	10.8	+ 79.2	+ 74.0	— 75.1	— 78.5	+ 2.5	— 31	— 1
30	" 15	1.9	+ 77.3	+ 74.3	— 73.7	— 78.0	+ 1.5	+ 25	0
31	" 16	8.4	+ 76.6	+ 74.6	— 73.4	— 76.6	+ 1.3	+ 18	+ 4
32	" 20	14.2	— 108.0	— 282.3	+ 283.8	+ 112.3	+ 88.6	+ 1206	+ 20
33	" 21	14.1	+ 54.3	— 117.6	+ 121.3	— 51.1	+ 87.7	+ 1201	+ 24
34	" 27	12.4	— 112.0	— 283.2	+ 283.9	+ 113.6	+ 85.9	+ 1190	+ 7
35	Oct. 10	12.8	+ 140.5	— 29.4	+ 33.2	— 138.4	+ 86.4	+ 1192	+ 22
36	" 14	11.4	+ 176.6	+ 5.2	— 6.0	— 174.4	+ 83.6	+ 1186	+ 6
37	" 17	12.3	+ 125.6	— 45.3	+ 47.4	— 123.7	+ 86.4	+ 1193	+ 14
38	" 25	11.8	— 112.0	— 284.5	+ 282.5	+ 115.1	+ 86.5	+ 1186	+ 4

These results have next been compared with Bessel's refractions by the aid of Table X. This gives the mean refraction for altitudes of every 100'' from the horizon to 5°, for a temperature of 48°.8 and a barometric pressure of 29.6 inches. The altitude corresponding to any refraction given in the table is found by adding the argument at the top of the column to that given in the first column, all the quantities being expressed in seconds of arc. Thus the refraction 1815'' corresponds to the altitude 1400'', 618'' to 16900'', etc.

After applying the corrections for temperature and pressure of the air to each observation, the residuals have been found by subtracting

TABLE XI.—NUMBER OF OBSERVATIONS.

from them the refraction as given by Bessel. These residuals are arranged in groups in Tables XI. and XII. Each group extends over  $10'$ , its central point being given in the first columns. Table XI. gives the number of residuals contained in each group, and Table XII. their mean value. The corresponding number of the series is given at the top of each column. The measures of the upper and lower limbs of the sun are combined, as there seems to be no systematic difference between them. Series 7 is omitted, since there is an error in the number of turns of the micrometer screw, or in the number of minutes in the observed times.

The results of these two tables are combined in Table XIII. The successive columns give the altitude, the corresponding refraction according to Bessel, the total number of observations of the sun, and of *a Bootis*. The next two columns are derived from Table XII., and give the means of the residuals contained in that table relating to the sun, and the means of those relating to *a Bootis*.

TABLE XII.—MEAN RESIDUALS.

[illegible]

TABLE XIII.

Alt.	Bessel Ref.	No.		Mean.	
		s.	a.	s.	a.
0 20	1852	1	..	-173	..
30	1744	6	..	-111	..
40	1643	20	4	-122	+ 6
50	1550	48	5	-105	- 4
1 0	1465	46	5	-107	-26
10	1387	35	7	-104	-24
20	1316	24	8	- 91	-34
30	1251	21	11	- 78	-13
40	1192	26	13	- 83	-24
50	1138	28	14	- 92	-14
2 0	1089	18	18	- 78	-17
10	1043	18	16	- 66	-17
20	1001	13	21	- 47	-19
30	961	13	17	- 59	- 6
40	923	13	15	- 65	- 8
50	888	19	14	- 58	- 6
3 0	855	17	15	- 66	- 2
10	824	15	18	- 69	+ 8
20	795	10	18	- 51	+ 8
30	768	9	17	- 41	+ 9
40	744	8	16	- 45	+25
50	721	5	11	- 39	+17
4 0	699	5	10	- 40	+17
10	678	..	5	..	+11
20	659	..	3	..	+36
30	640	..	3	..	+37
40	621	..	4	..	+44
50	603	..	1	..	+22

The fact noticed by Argelander, that the refraction derived from the setting sun is less than that of a star is well shown in this table. The difference amounts to one or two minutes of arc.

In this investigation the value of one division of the screw in seconds must be known with accuracy. It was therefore redetermined August 6, 1885, with the same result,  $13''.95$ , as that originally found.

This paper is intended to show that the micrometer level is capable of giving useful results where a larger instrument has generally been considered necessary. Its portability, and the rapidity with which observations may be made by it, adapt it especially to the wants of travellers, and would permit the accumulation of valuable information regarding the atmospheric conditions of comparatively inaccessible points. If required, much greater accuracy could doubtless be attained than is indicated by the stellar observations described above. The instrument was mounted on a wooden balcony, and the times were only taken to whole seconds. Instead of moving the telescope each

time, it might be better to have a series of lines in the field, and observe the transits over each, as in a meridian instrument. The advantages of the two forms of instrument employed, attaching the level to the telescope or to the wyes, will vary with the surrounding conditions. The principal objection to the second method is the time required to determine the constants. This may be done almost equally well when the level is attached directly to the telescope, by taking reciprocal readings from two points one or two hundred yards apart. The variations of the instrumental constants will also doubtless be less with this form of instrument. In either case, if many observations are to be taken from a given station, it is advisable to determine once for all the absolute altitude of some convenient object, and refer everything to that, like the meridian mark of a transit instrument.

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## XVII.

## A NEW FORM OF POLARIMETER.

BY EDWARD C. PICKERING.

Presented May 26, 1885.

Two instruments have been proposed for measuring the relative intensity of the components of a ray of polarized light. First, the Arago polarimeter, in which a number of glass plates are placed in front of a Savart polariscope, and may be inclined at any desired angle. Bands are produced by the Savart plate, which are made to disappear by inclining the plates so as to neutralize the polarization of the beam. The inclination of the plates is a measure of the intensity of the polarization. Secondly, a polarimeter was devised by the writer,\* in which the light is admitted through a rectangular aperture, two juxtaposed images of which are formed by a double-image prism. If the light is polarized, the two rectangles will be of unequal brightness. Interposing a Nicol prism, the two images may always be rendered equal by rotating the Nicol. The intensity of the polarization is measured by the cosine of the angle of rotation. The principal objection to the Arago polarimeter is, that the law connecting the inclination of the plates and the amount of polarization is extremely complex, and is best determined experimentally in each case. This instrument is also ill adapted to measure a ray which is almost perfectly polarized, but when the polarization is slight, the well-known sensitiveness of the Savart bands renders the accidental errors small. The other form of polarimeter is open to the objection that it is not very sensitive when the polarization is slight. On the other hand, the amount of polarization is directly connected with the angle of rotation of the prism by a simple formula, and when a ray is strongly polarized it gives excellent results.

The advantages of both instruments appear to be combined in the following modification of the second instrument. The greater sensi-

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\* Proc. Amer. Acad., IX. 1.

tiveness of the Arago polarimeter seems to be due to the fact, that, instead of comparing the brightness of the field on two sides of the line separating them, the comparison may be made on both sides of each band, or throughout nearly the whole field. Accordingly, the rectangular aperture was replaced by a series of metallic bars separated by intervals exactly equal to their width. The double-image prism is then placed at such a distance that the separation of the images shall equal the width of the bars, so that the two images of the intervals shall be exactly in contact. If this condition is fulfilled, the bands will disappear, and the field will be perfectly uniform when the Nicol is turned so that the two images have equal intensity. A slight motion of the Nicol will render the bands alternately light and dark, and the exact point of disappearance may be determined with much precision. The sensitiveness appears to be even greater than that of the Savart plate, since the change in brightness is abrupt at the edges of the band, instead of varying continuously from the centre of the band to the centre of the interspace. The bands were made by cementing a piece of tin-foil to a plate of glass, ruling a series of parallel lines upon it, and removing the foil from the space between the second and third, and the fourth and fifth lines, &c. It was necessary that these intervals should be made less than the interval between the first and second, and the third and fourth lines, &c., by the width of the line cut in the foil; otherwise the bands would be narrower than the interspaces by this amount. The bands might also be sawed out of a plate of brass, and finished with a file. Since the separation of the images produced by Iceland spar varies with the angular direction of the ray traversing it, the bands will not disappear in all parts of the field at once. This, however, is rather an advantage, since the eye is extremely sensitive to a certain phase, in which the bands reappear equally in the two sides of the field. A pointer serves to guide the eye to the centre of the field. Should it be desirable to employ a large field, the rays may be rendered parallel by a convex lens at a distance from the eye equal to its focal distance. There are some advantages in substituting a simple plate of Iceland spar for the double-image prism. The rays compared then come in the same direction, instead of being inclined by an angle equal to that of the images of the prism. The two images do not lie in the same plane. This may be remedied by inclining the bars so that the right-hand edges shall always be in front or behind the left-hand edges. If, however, the bands are narrow, and are placed at the distance of distinct vision, this error is unimportant, and the bands may be made to disappear almost entirely.

In the paper referred to above, it was shown that the polarization

Table I. serves to reduce the observations. The argument gives the sum of the two differences found by subtracting the first reading from the second, and the third from the fourth. The tabular number gives the corresponding polarization. If the sum of the differences exceeds  $180^\circ$ , it must be subtracted from  $360^\circ$ . This may be avoided by beginning with the second reading.

TABLE I.—REDUCTION TABLE.

[illegible]

TABLE I.—*Continued.*

2v	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
15	99.1	99.1	99.1	99.1	99.1	99.1	99.1	99.1	99.0	99.0
16	99.0	99.0	99.0	99.0	99.0	99.0	99.0	99.0	98.9	98.9
17	98.9	98.9	98.9	98.9	98.8	98.8	98.8	98.8	98.8	98.8
18	98.8	98.8	98.7	98.7	98.7	98.7	98.7	98.7	98.7	98.6
19	98.6	98.6	98.6	98.6	98.6	98.6	98.5	98.5	98.5	98.5
20	98.5	98.5	98.4	98.4	98.4	98.4	98.4	98.4	98.4	98.3
21	98.3	98.3	98.3	98.3	98.3	98.2	98.2	98.2	98.2	98.2
22	98.2	98.1	98.1	98.1	98.1	98.1	98.1	98.0	98.0	98.0
23	98.0	98.0	98.0	97.9	97.9	97.9	97.9	97.9	97.8	97.8
24	97.8	97.8	97.8	97.8	97.7	97.7	97.7	97.7	97.7	97.6
25	97.6	97.6	97.6	97.6	97.6	97.5	97.5	97.5	97.5	97.5
26	97.4	97.4	97.4	97.4	97.4	97.3	97.3	97.3	97.3	97.3
27	97.2	97.2	97.2	97.2	97.2	97.1	97.1	97.1	97.1	97.0
28	97.0	97.0	97.0	97.0	96.9	96.9	96.9	96.9	96.9	96.8
29	96.8	96.8	96.8	96.7	96.7	96.7	96.7	96.7	96.6	96.6
30	96.6	96.6	96.5	96.5	96.5	96.5	96.5	96.4	96.4	96.4
31	96.4	96.3	96.3	96.3	96.3	96.2	96.2	96.2	96.2	96.2
32	96.1	96.1	96.1	96.1	96.0	96.0	96.0	96.0	95.9	95.9
33	95.9	95.9	95.8	95.8	95.8	95.8	95.7	95.7	95.7	95.7
34	95.6	95.6	95.6	95.6	95.5	95.5	95.5	95.4	95.4	95.4
35	95.4	95.3	95.3	95.3	95.3	95.2	95.2	95.2	95.2	95.1
36	95.1	95.1	95.1	95.0	95.0	95.0	94.9	94.9	94.9	94.9
37	94.8	94.8	94.8	94.8	94.7	94.7	94.7	94.6	94.6	94.6
38	94.6	94.5	94.5	94.5	94.4	94.4	94.4	94.4	94.3	94.3
39	94.3	94.2	94.2	94.2	94.2	94.1	94.1	94.1	94.0	94.0
40	94.0	93.9	93.9	93.9	93.8	93.8	93.8	93.8	93.7	93.7
41	93.7	93.6	93.6	93.6	93.5	93.5	93.5	93.4	93.4	93.4
42	93.4	93.3	93.3	93.3	93.2	93.2	93.2	93.1	93.1	93.1
43	93.0	93.0	93.0	92.9	92.9	92.9	92.8	92.8	92.8	92.8
44	92.7	92.7	92.7	92.6	92.6	92.6	92.5	92.5	92.5	92.4
45	92.4	92.4	92.3	92.3	92.3	92.2	92.2	92.2	92.1	92.1
46	92.0	92.0	92.0	91.9	91.9	91.9	91.8	91.8	91.8	91.7
47	91.7	91.7	91.6	91.6	91.6	91.5	91.5	91.5	91.4	91.4
48	91.4	91.3	91.3	91.2	91.2	91.2	91.1	91.1	91.1	91.0
49	91.0	91.0	90.9	90.9	90.8	90.8	90.8	90.7	90.7	90.7
50	90.6	90.6	90.6	90.5	90.5	90.4	90.4	90.4	90.3	90.3
51	90.3	90.2	90.2	90.1	90.1	90.1	90.0	90.0	90.0	89.9
52	89.9	89.8	89.8	89.8	89.7	89.7	89.6	89.6	89.6	89.5
53	89.5	89.4	89.4	89.4	89.3	89.3	89.3	89.2	89.2	89.1
54	89.1	89.1	89.0	89.0	88.9	88.9	88.9	88.8	88.8	88.7
55	88.7	88.7	88.6	88.6	88.5	88.5	88.5	88.4	88.4	88.3
56	88.3	88.2	88.2	88.2	88.1	88.1	88.0	88.0	88.0	87.9
57	87.9	87.8	87.8	87.8	87.7	87.7	87.6	87.6	87.5	87.5
58	87.5	87.4	87.4	87.3	87.3	87.2	87.2	87.2	87.1	87.1
59	87.0	87.0	87.0	86.9	86.9	86.8	86.8	86.7	86.7	86.6
60	86.6	86.6	86.5	86.5	86.4	86.4	86.3	86.3	86.2	86.2
61	86.2	86.1	86.1	86.0	86.0	85.9	85.9	85.9	85.8	85.8
62	85.7	85.7	85.6	85.6	85.5	85.5	85.4	85.4	85.4	85.3
63	85.3	85.2	85.2	85.1	85.1	85.0	85.0	84.9	84.9	84.8
64	84.8	84.8	84.7	84.7	84.6	84.6	84.5	84.5	84.4	84.4
65	84.3	84.3	84.2	84.2	84.2	84.1	84.1	84.0	84.0	83.9
66	83.9	83.8	83.8	83.7	83.7	83.6	83.6	83.5	83.5	83.4
67	83.4	83.3	83.3	83.2	83.2	83.1	83.1	83.0	83.0	83.0
68	82.9	82.9	82.8	82.8	82.7	82.7	82.6	82.6	82.5	82.5
69	82.4	82.4	82.3	82.3	82.2	82.2	82.1	82.1	82.0	82.0

TABLE I.—Continued.

2v	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
70	81.9	81.9	81.8	81.8	81.7	81.7	81.6	81.6	81.5	81.5
71	81.4	81.4	81.3	81.3	81.2	81.2	81.1	81.1	81.0	81.0
72	80.9	80.9	80.8	80.7	80.7	80.6	80.6	80.5	80.5	80.4
73	80.4	80.3	80.3	80.2	80.2	80.1	80.1	80.0	80.0	79.9
74	79.9	79.8	79.8	79.7	79.6	79.6	79.5	79.5	79.4	79.4
75	79.3	79.3	79.2	79.2	79.1	79.1	79.0	79.0	78.9	78.9
76	78.8	78.7	78.7	78.6	78.6	78.5	78.5	78.4	78.4	78.3
77	78.3	78.2	78.2	78.1	78.0	78.0	77.9	77.9	77.8	77.8
78	77.7	77.7	77.6	77.5	77.5	77.4	77.4	77.3	77.3	77.2
79	77.2	77.1	77.0	77.0	76.9	76.9	76.8	76.8	76.7	76.7
80	76.6	76.5	76.5	76.4	76.4	76.3	76.3	76.2	76.2	76.1
81	76.0	76.0	75.9	75.9	75.8	75.8	75.7	75.6	75.6	75.5
82	75.5	75.4	75.4	75.3	75.2	75.2	75.1	75.1	75.0	75.0
83	74.9	74.8	74.8	74.7	74.7	74.6	74.6	74.5	74.4	74.4
84	74.3	74.3	74.2	74.1	74.1	74.0	74.0	73.9	73.8	73.8
85	73.7	73.7	73.6	73.6	73.5	73.4	73.4	73.3	73.2	73.2
86	73.1	73.1	73.0	73.0	72.9	72.8	72.8	72.7	72.7	72.6
87	72.5	72.5	72.4	72.4	72.3	72.2	72.2	72.1	72.1	72.0
88	71.9	71.9	71.8	71.8	71.7	71.6	71.6	71.5	71.4	71.4
89	71.3	71.3	71.2	71.1	71.1	71.0	71.0	70.9	70.8	70.8
90	70.7	70.6	70.6	70.5	70.5	70.4	70.3	70.3	70.2	70.2
91	70.1	70.0	70.0	69.9	69.8	69.8	69.7	69.7	69.6	69.5
92	69.5	69.4	69.3	69.3	69.2	69.1	69.1	69.0	69.0	68.9
93	68.8	68.8	68.7	68.6	68.6	68.5	68.4	68.4	68.3	68.3
94	68.2	68.1	68.1	68.0	67.9	67.9	67.8	67.8	67.7	67.6
95	67.6	67.5	67.4	67.4	67.3	67.2	67.2	67.1	67.0	67.0
96	66.9	66.8	66.8	66.7	66.6	66.6	66.5	66.5	66.4	66.3
97	66.3	66.2	66.1	66.1	66.0	65.9	65.9	65.8	65.7	65.7
98	65.6	65.5	65.5	65.4	65.3	65.3	65.2	65.1	65.1	65.0
99	64.9	64.9	64.8	64.7	64.7	64.6	64.6	64.5	64.4	64.3
100	64.3	64.2	64.1	64.1	64.0	63.9	63.9	63.8	63.7	63.7
101	63.6	63.5	63.5	63.4	63.3	63.3	63.2	63.1	63.1	63.0
102	62.9	62.9	62.8	62.7	62.7	62.6	62.5	62.5	62.4	62.3
103	62.2	62.2	62.1	62.0	62.0	61.9	61.8	61.8	61.7	61.6
104	61.6	61.5	61.4	61.4	61.3	61.2	61.2	61.1	61.0	60.9
105	60.9	60.8	60.7	60.7	60.6	60.5	60.5	60.4	60.3	60.2
106	60.2	60.1	60.0	60.0	59.9	59.8	59.8	59.7	59.6	59.6
107	59.5	59.4	59.3	59.3	59.2	59.1	59.1	59.0	58.9	58.8
108	58.8	58.7	58.6	58.6	58.5	58.4	58.4	58.3	58.2	58.1
109	58.1	58.0	57.9	57.9	57.8	57.7	57.7	57.6	57.5	57.4
110	57.4	57.3	57.2	57.1	57.1	57.0	56.9	56.9	56.8	56.7
111	56.6	56.6	56.5	56.4	56.4	56.3	56.2	56.1	56.1	56.0
112	55.9	55.8	55.8	55.7	55.6	55.6	55.5	55.4	55.3	55.3
113	55.2	55.1	55.0	55.0	54.9	54.8	54.8	54.7	54.6	54.5
114	54.5	54.4	54.3	54.2	54.2	54.1	54.0	54.0	53.9	53.8
115	53.7	53.7	53.6	53.5	53.4	53.4	53.3	53.2	53.2	53.1
116	53.0	52.9	52.8	52.8	52.7	52.6	52.6	52.5	52.4	52.3
117	52.2	52.2	52.1	52.0	52.0	51.9	51.8	51.7	51.6	51.6
118	51.5	51.4	51.4	51.3	51.2	51.1	51.0	51.0	50.9	50.8
119	50.8	50.7	50.6	50.5	50.4	50.4	50.3	50.2	50.2	50.1
120	50.0	49.9	49.8	49.8	49.7	49.6	49.5	49.5	49.4	49.3
121	49.2	49.2	49.1	49.0	48.9	48.9	48.8	48.7	48.6	48.6
122	48.5	48.4	48.3	48.2	48.2	48.1	48.0	47.9	47.9	47.8
123	47.7	47.6	47.6	47.5	47.4	47.3	47.2	47.2	47.1	47.0
124	47.0	46.9	46.8	46.7	46.6	46.6	46.5	46.4	46.3	46.2

TABLE I.—*Continued.*

2 v	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
125	46.2	46.1	46.0	45.9	45.9	45.8	45.7	45.6	45.6	45.5
126	45.4	45.3	45.2	45.2	45.1	45.0	44.9	44.9	44.8	44.7
127	44.6	44.5	44.5	44.4	44.3	44.2	44.2	44.1	44.0	43.9
128	43.8	43.8	43.7	43.6	43.5	43.4	43.4	43.3	43.2	43.1
129	43.0	43.0	42.9	42.8	42.7	42.7	42.6	42.5	42.4	42.3
130	42.3	42.2	42.1	42.0	41.9	41.9	41.8	41.7	41.6	41.6
131	41.5	41.4	41.3	41.2	41.2	41.1	41.0	40.9	40.8	40.8
132	40.7	40.6	40.5	40.4	40.4	40.3	40.2	40.1	40.0	40.0
133	39.9	39.8	39.7	39.6	39.6	39.5	39.4	39.3	39.2	39.2
134	39.1	39.0	38.9	38.8	38.8	38.7	38.6	38.5	38.4	38.4
135	38.3	38.2	38.1	38.0	37.9	37.9	37.8	37.7	37.6	37.5
136	37.5	37.4	37.3	37.2	37.1	37.1	37.0	36.9	36.8	36.7
137	36.6	36.6	36.5	36.4	36.3	36.2	36.2	36.1	36.0	35.9
138	35.8	35.8	35.7	35.6	35.5	35.4	35.3	35.3	35.2	35.1
139	35.0	34.9	34.9	34.8	34.7	34.6	34.5	34.4	34.4	34.3
140	34.2	34.1	34.0	34.0	33.9	33.8	33.7	33.6	33.5	33.5
141	33.4	33.3	33.2	33.1	33.0	33.0	32.9	32.8	32.7	32.6
142	32.6	32.5	32.4	32.3	32.2	32.1	32.1	32.0	31.9	31.8
143	31.7	31.6	31.6	31.5	31.4	31.3	31.2	31.1	31.1	31.0
144	30.9	30.8	30.7	30.7	30.6	30.4	30.4	30.3	30.2	30.2
145	30.1	30.0	29.9	29.8	29.7	29.6	29.6	29.5	29.4	29.3
146	29.2	29.2	29.1	29.0	28.9	28.8	28.7	28.6	28.6	28.5
147	28.4	28.3	28.2	28.1	28.1	28.0	27.9	27.8	27.7	27.6
148	27.6	27.5	27.4	27.3	27.2	27.1	27.1	27.0	26.9	26.8
149	26.7	26.6	26.6	26.5	26.4	26.3	26.2	26.1	26.0	26.0
150	25.9	25.8	25.7	25.6	25.5	25.4	25.4	25.3	25.2	25.1
151	25.0	25.0	24.9	24.8	24.7	24.6	24.5	24.4	24.3	24.2
152	24.2	24.1	24.0	23.9	23.8	23.8	23.7	23.6	23.5	23.4
153	23.3	23.3	23.2	23.1	23.0	22.9	22.8	22.7	22.7	22.6
154	22.5	22.4	22.3	22.3	22.2	22.1	22.0	21.9	21.8	21.7
155	21.6	21.5	21.5	21.4	21.3	21.2	21.1	21.0	21.0	20.9
156	20.8	20.7	20.6	20.5	20.4	20.4	20.3	20.2	20.1	20.0
157	19.9	19.9	19.8	19.7	19.6	19.5	19.4	19.3	19.2	19.2
158	19.1	19.0	18.9	18.8	18.7	18.7	18.6	18.5	18.4	18.3
159	18.2	18.1	18.0	18.0	17.9	17.8	17.7	17.6	17.5	17.4
160	17.4	17.3	17.2	17.1	17.0	16.9	16.8	16.8	16.7	16.6
161	16.5	16.4	16.3	16.2	16.2	16.1	16.0	15.9	15.8	15.7
162	15.6	15.6	15.5	15.4	15.3	15.2	15.1	15.0	15.0	14.9
163	14.8	14.7	14.6	14.5	14.4	14.3	14.3	14.2	14.1	14.0
164	13.9	13.8	13.7	13.7	13.6	13.5	13.4	13.3	13.2	13.1
165	13.1	13.0	12.9	12.8	12.7	12.6	12.5	12.4	12.4	12.3
166	12.2	12.1	12.0	11.9	11.8	11.8	11.7	11.6	11.5	11.4
167	11.3	11.2	11.2	11.1	11.0	10.9	10.8	10.7	10.6	10.5
168	10.4	10.4	10.3	10.2	10.1	10.0	9.9	9.8	9.8	9.7
169	9.6	9.5	9.4	9.3	9.2	9.1	9.1	9.0	8.9	8.8
170	8.7	8.6	8.5	8.5	8.4	8.3	8.2	8.1	8.0	7.9
171	7.8	7.8	7.7	7.6	7.5	7.4	7.3	7.2	7.1	7.1
172	7.0	6.9	6.8	6.7	6.6	6.5	6.5	6.4	6.3	6.2
173	6.1	6.0	5.9	5.8	5.8	5.7	5.6	5.5	5.4	5.3
174	5.2	5.1	5.1	5.0	4.9	4.8	4.7	4.6	4.5	4.5
175	4.4	4.3	4.2	4.1	4.0	3.9	3.8	3.8	3.7	3.6
176	3.5	3.4	3.3	3.2	3.1	3.1	3.0	2.9	2.8	2.7
177	2.6	2.5	2.4	2.4	2.3	2.2	2.1	2.0	1.9	1.8
178	1.7	1.7	1.6	1.5	1.4	1.3	1.2	1.1	1.0	1.0
179	0.9	0.8	0.7	0.6	0.5	0.4	0.4	0.3	0.2	0.1

TABLE II. — OBSERVATIONS.

No.	Date.	G. M. T.	Dist.	Table of Quantities.	No.	Date.	G. M. T.	Dist.	Table of Quantities.
	1884.	h. m.	°			1885.	h. m.	°	
1	Aug. 1	11 58	90	21.7	45	July 15	13 58	90	13.3
2	"	11 59	90	24.2	46	"	14 3	90	12.6
3	"	12 2	90	25.1	47	"	5	90	9.1
4	"	4	90	30.7	48	July 21	16 13	90	39.2
5	"	9	90	36.0	49	"	16	90	36.5
6	"	16	90	43.6	50	"	18	90	39.8
7	"	17	90	44.4	51	July 27	16 5	90	50.2
8	"	20	90	44.6	52	"	18	90	49.2
9	"	25	90	45.9	53	"	23	90	49.4
10	"	29	90	40.4	54	July 28	15 40	90	51.4
11	"	34	90	48.2	55	"	41	90	48.9
12	Aug. 2	9 40	90	45.6	56	"	43	90	49.9
13	"	42	90	45.3	57	"	55	15	21.1
14	"	44	75	36.6	58	"	58	30	6.8
15	"	47	60	37.4	59	"	16 1	45	10.1
16	"	50	45	9.6	60	"	4	60	22.6
17	"	52	30	6.4	61	"	9	75	42.1
18	"	54	15	0.4	62	"	11	90	50.1
19	"	56	60	15.1	63	"	14	105	40.6
20	"	10 1	90	29.6	64	"	17	120	21.6
21	"	8	90	29.2	65	"	84	105	38.8
22	Sept. 13	10 48	90	33.6	66	"	40	90	50.1
23	"	49	90	34.0	67	"	42	75	43.0
24	"	51	90	35.3	68	"	45	60	27.1
25	"	52	90	38.3	69	"	48	45	15.6
26	"	54	90	39.1	70	"	50	30	10.4
27	"	11 0	90	47.9	71	"	53	15	13.2
28	"	1	90	48.8	72	Sept. 21	16 5	90	58.8
29	"	3	90	49.5	73	"	7	90	60.7
30	"	10	90	58.2	74	"	9	90	59.1
31	"	12	90	59.3	75	"	14	15	16.6
32	"	14	90	58.8	76	"	17	30	2.3
33	"	16	90	58.3	77	"	20	45	12.6
34	Nov. 18	17 40	90	40.5	78	"	23	60	31.6
	1885.				79	"	27	75	50.8
35	June 6	14 22	90	37.9	80	"	30	90	57.0
36	"	24	90	41.4	81	"	32	105	54.8
37	"	25	90	36.5	82	"	35	120	38.8
38	June 14	10 24	90	44.2	83	"	42	105	53.2
39	"	55	90	50.7	84	"	44	90	60.5
40	"	58	90	52.6	85	"	46	75	49.0
41	"	11 0	90	52.2	86	"	48	60	29.8
42	July 1	4 32	90	45.8	87	"	51	45	11.8
43	"	35	90	45.3	88	"	53	30	1.5
44	"	36	90	45.3	89	"	55	15	16.1

The use of this polarimeter is shown in Table II., which gives some illustrations of its application to the study of atmospheric polarization. All these observations are made in the vertical plane passing through the sun. The successive columns give a number for reference, the

date, the Greenwich mean time, the angular distance of the point observed from the sun, and the resulting polarization. The first 44 sets were made by myself, the others by Miss N. A. Farrar.

Nos. 1 to 11 were made on the zenith after sunset. The later observations were difficult on account of the increasing darkness. On reducing the observations, an unexpected result was attained. The last column shows that the polarization increases regularly, becoming twice as great at the end as at the beginning of the series. The probable explanation of this phenomenon is, that after the sun has set the light reaching us from the zenith comes from the upper portions of the atmosphere. As this is presumably clearer, and more free from dust and haze, we should anticipate a more complete polarization. It affords a simple means of determining the effect of ascending to various heights above the surface of the earth. From the distance of the sun below the horizon these heights are readily calculated. Nos. 22 to 33 were made in the same way, and afford a confirmation of these results. The measures on August 1 are probably somewhat too small, owing to an inclination of the bars to the plane of polarization. On August 2, the sky was clear, but hazy around the sun. The observations were abandoned owing to the approach of cirrus clouds, which probably caused the diminution in the amount of the polarization. On September 13, the air was very clear. No satisfactory explanation appears for the small amount of polarization on July 15. The record states that clouds interfered with set 45, but that it was clear when sets 46 and 47 were taken. The bars may not have been set parallel to the plane of polarization, as it was the first time the observer had used the instrument.

The law determining the amount of polarization at different distances from the sun is indicated by the observations made on July 28 and on September 21. On the first date, the remark occurs, "Sky hazy," and on the second, "Sky entirely clear." The greater polarization on the latter date is doubtless due to this cause. Both sets show the maximum polarization at  $90^\circ$ . They also indicate a greater polarization at  $15^\circ$  than at  $30^\circ$ . This may be due to Babinet's neutral point; but in that case we should anticipate a negative polarization at  $15^\circ$ . Probably these sets are uncertain, on account of the proximity of the sun.

One of the most important applications of this polarimeter will be as a measure of the haziness of the air. As the polarization becomes insensible when the sky is entirely overcast, we apparently have a very delicate test for the amount of haze. Simultaneous observations of a

distant mountain would be particularly valuable in this connection, as a means of comparing the polarization of the sky with that of the light received from the mountain. The relative intensity of the light from the mountain and the adjacent sky should also be compared, since this quantity would also vary with the clearness of the air. All of these quantities are readily measured with this instrument. To compare the light of the sky with that received from the mountain, it is only necessary to conceal the sky line behind one of the bars, and thus compare the relative intensities of the two rays. As the vertical component of one ray will be compared with the horizontal component of the other ray, the relative intensities will be modified by the amount of the polarization. The observation should therefore be repeated, placing the sky line of the mountain behind one of the adjacent bars. The polarization of the light received from the sky and the mountain should also be determined, and we can then determine the relative intensities of the four components. These measurements will be made more readily if the polarimeter is inserted in the eyepiece of a telescope of low power, placing the bars in the focus and the double-image prism between them and the field lens. The Nicol may be placed between the field and eye lenses, or between the eye lens and the eye.

## XVIII.

## A NEW LOGICAL MACHINE.

BY ALLAN MARQUAND, PH. D.

Presented by Invitation, November 11, 1885.

DURING the year 1881 I constructed a logical machine somewhat similar to the well-known machine of Prof. Jevons, and printed logical diagrams for problems involving as many as ten terms.\* This earlier instrument and the logical diagrams formed the basis of the machine illustrated on the accompanying plate. The new machine was constructed in Princeton during the winter of 1881-82, by my friend Prof. C. G. Rockwood, Jr., whose mechanical skill and untiring patience gave me invaluable assistance. The machine was made from the wood of a red-cedar post, which once formed part of the enclosure of Princeton's oldest homestead. It measures 32 cm. high by 21 cm. wide and 15 cm. deep. Like the instrument of Prof. Jevons, and that of Prof. Venn, it is constructed for problems involving only four terms, but more readily than either of those instruments admits of being extended for problems involving a larger number of terms.

The face of the machine (Fig. I.) presents to view sixteen small pointers representing the sixteen logical combinations of the symbols *A*, *B*, *C*, and *D*, with their negatives *a*, *b*, *c*, *d*. These combinations are so arranged that all the *A* combinations are found in the two vertical columns to our left, the *a* combinations in the two vertical columns to the right. The *A* combinations are subdivided vertically into the *B* and *b* combinations, and the *a* series in like manner. Both are also subdivided horizontally into the *C* and *c* combinations, and each of these again into the *D* and *d* combinations. Thus the uppermost pointer to the left represents the combination *A B C D*, the horizontally adjoining one *A b C D*, the next *a B C D*, and so on until we reach the lowermost to the right, which is *a b c d*. Below the pointers may be seen the two operation keys marked 1 and 0, and the four positive and four negative letter keys under their respective symbols.

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\* *Philos. Mag.*, October, 1881, pp. 266-270.

The *I* key may be called the *restoration key*. It prepares the machine for a new problem, by raising all the pointers to the horizontal position. The *O* key may be called the *destruction key*, as when pressed down it allows the pointers to fall. The function of a *letter key* is to sustain in the horizontal position the pointers representing the corresponding negative combinations. Thus, if the *A* key is pressed, the *a* pointers are sustained; if the *b* key is pressed, the *B* pointers are sustained; and similarly for all the remaining letter keys.

Turning now to Fig. II., the mechanism by which this is effected will be easily seen. On the inner face of the machine, and corresponding to the pointers, are sixteen drops, some of which are pictured in the horizontal position, and some as fallen. The two operation keys move rectangular frameworks, each consisting of four vertical brass rods fastened together, and carrying pins which reach all of the sixteen drops. The framework of the *O* key moves on the inner, that of the *I* key on the outer side of the drops, both horizontally. If we wish to bring all the pointers to the horizontal position and hold them there, both operation keys are pressed down. The *I* key raises all the drops. Releasing first the *O* key, its framework is drawn back by a fixed spring, and by means of its pins holds the drops in position; on releasing the *I* key, its framework is drawn back so as not to interfere with subsequent operations. Each letter key operates two vertical or two horizontal rods, free to revolve on their axes. In each rod are set four pins, conveniently bent, so that when the rods are partially revolved, by pressure of the letter keys, the pins are made to sustain the drops in the horizontal position without raising those which have fallen. The rods return to their original position, by means of small spiral springs, as soon as the pressure of the letter keys is released. The desired motion is communicated to the rods by means of cat-gut strings, there being two such strings from each letter key. Thus the *A* key operates the two vertical rods which are to hold the *a* drops; the *b* key the rods for holding the *B* drops; and the other letter keys in like manner. By this device it will be seen that, if we should press the *A* key (this holds the *a* combinations), and then the *O* key, only the *A* pointers will fall; or, if both the *A* and *B* keys are depressed (this holds the *a* and *b* combinations), and then the *O* key, only the *A B* pointers will fall; and similarly for the other combinations.

To utilize the instrument for the solution of logical problems, we first raise all the pointers to the horizontal position. This will indicate the state of a logical universe of four terms before the introduction of premises. Now, since the establishment of any combination



Fig. I.

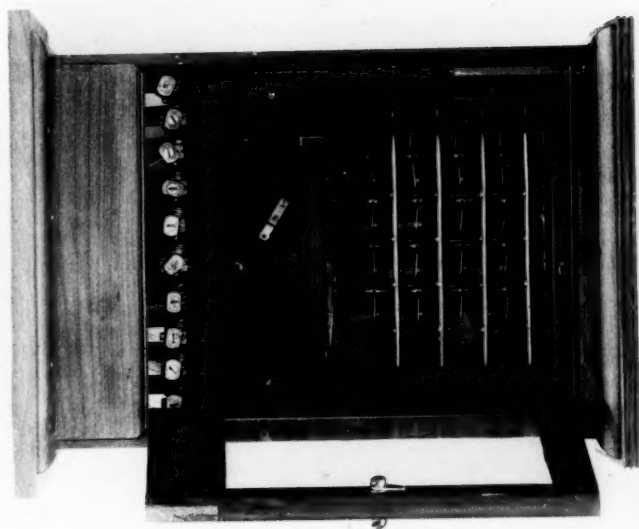
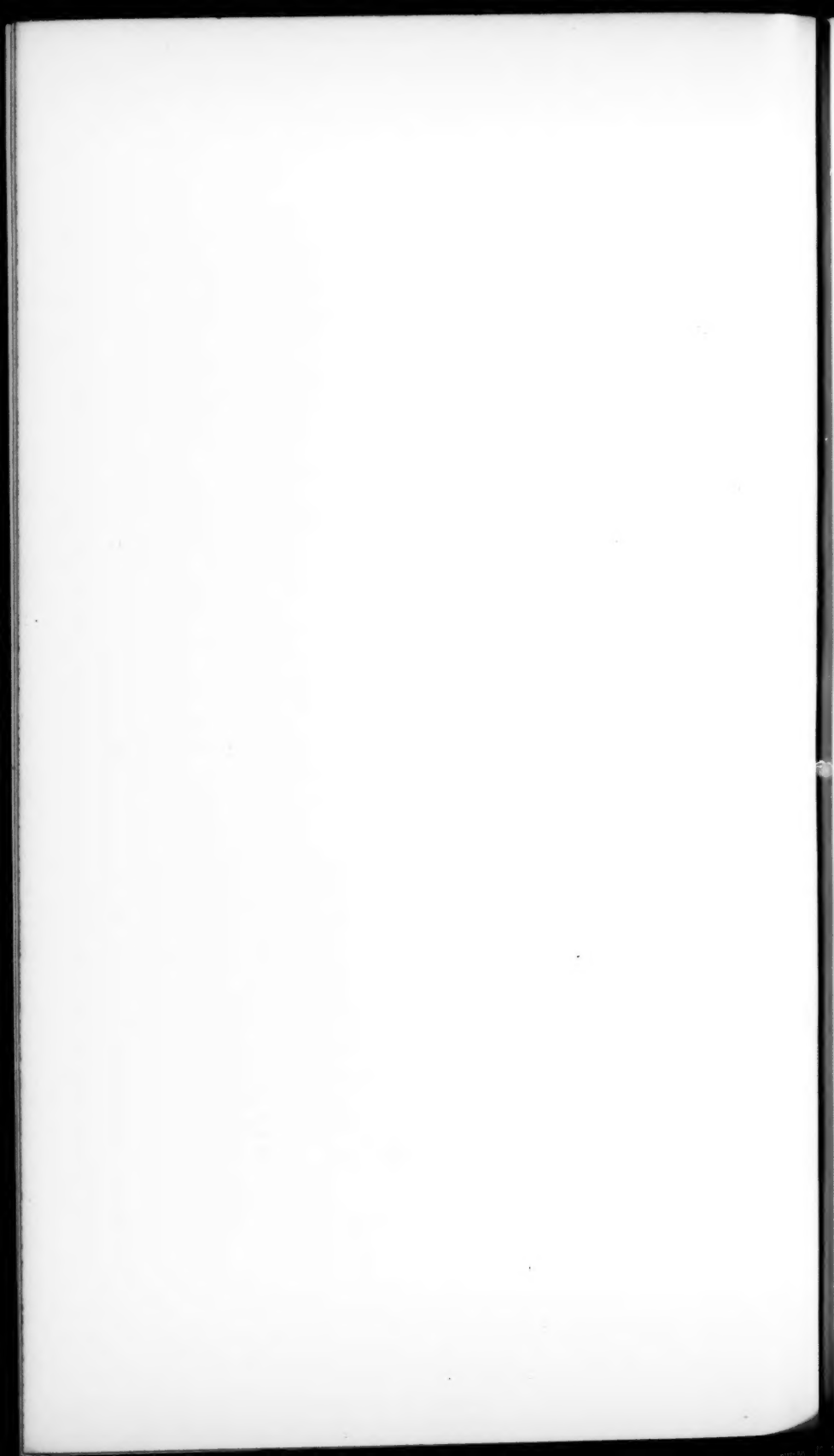


Fig. II.



means the negation of some other, we may express our premises in negative form. Thus, in general,  $A \prec B$  (every  $A$  is  $B$ ) may be expressed  $A b \prec 0$  ( $A$ 's which are  $b$  do not exist). This we express upon our machine by pressing down the letter keys  $A$  and  $b$ , and then the destruction key. The falling of the  $A b$  pointers indicates exactly the change effected in the logical universe by the introduction of the premise  $A \prec B$ . We may then continue to impress as many premises as we please, until all the pointers have fallen. The following formulæ\* will suffice to illustrate the manner in which premises may be reduced from the positive to the negative form.

Positive Form.	Negative Form.
(1.) $A \prec B$ . . . . .	$A b \prec 0$ .
(2.) $A + B \prec C$ . . . . .	$\begin{cases} A c \prec 0. \\ B c \prec 0. \end{cases}$
(3.) $A \prec B + C$ . . . . .	$A b c \prec 0$ .
(4.) $A \prec b + C D$ . . . . .	$\begin{cases} A B c \prec 0. \\ A B d \prec 0. \end{cases}$
(5.) $A B \prec C$ . . . . .	$A B c \prec 0$ .
(6.) $A \prec B C$ . . . . .	$\begin{cases} A b \prec 0. \\ A c \prec 0. \end{cases}$
(7.) $A (B + C) \prec D$ . . . . .	$\begin{cases} A B d \prec 0. \\ A C d \prec 0. \end{cases}$
(8.) $A \prec B (C + D)$ . . . . .	$\begin{cases} A b \prec 0. \\ A c d \prec 0. \end{cases}$

Having expressed our premises upon the machine, and their effect being recorded by the pointers, it only remains for us to read off the conclusion. The entire conclusion is represented by the fallen pointers, and might be expressed as their joint sum; or it may be viewed as the logical sum of the combinations represented by the horizontal pointers. Thus, the premises of Barbara,  $A \prec B$  and  $B \prec C$ , give as the entire conclusion read negatively,

$$\left. \begin{array}{l} A b C \\ A b c \\ A B c \\ a B c \end{array} \right\} \prec 0.$$

\* The sign  $\prec$  is that used by Mr. C. S. Peirce for the general sign of inference.  $A \prec B$  means, if  $A$ , then  $B$ . Viewed in the light of class extension, it means the class  $A$  is included in the class  $B$ . The sign of addition is here used in the non-exclusive sense; thus,  $A + B$  means either  $A$  or  $B$ , or both. The expression  $AB$  means, when designating a class, the individuals which belong to both classes  $A$  and  $B$ ; when designating a quality, the combination of the qualities  $A$  and  $B$ .

Read positively, the conclusion is,

$$A B C + a B C + a b C + a b c = 1;$$

or, more briefly,

$$B C + a b = 1.$$

Ordinarily, the conclusion called for is part only of the total conclusion. Thus, syllogism with the above premises asks for a conclusion involving only  $A$  and  $C$ . An inspection of the dial-plate will show us the conclusion  $A < C$ , and also other conclusions involving relations between other terms than  $A$  and  $C$ ; thus,

$$c (A + B) < 0; b < a + c, \text{ etc.}$$

Nor is it necessary that our conclusions should be limited to relations between terms given in the premises, as may be seen in the solution of the following problems.

#### PROBLEM I.

Let us suppose that there are four girls at school, Anna, Bertha, Cora, and Dora, and that some one had observed that

(1.) Whenever either Anna or Bertha (or both) remained at home, Cora was at home; and

(2.) When Bertha was out, Anna was out; and

(3.) Whenever Cora was at home, Anna was at home.

What information is here conveyed concerning Dora?

Indicating by the capital letters the fact of *remaining at home*, and by the small letters that of *going out*, our premises are

$$A + B < C = \left. \begin{matrix} A c \\ B c \end{matrix} \right\} < 0$$

$$b < a = b A < 0$$

$$C < A = C a < 0$$

and, impressing them upon the machine, there will result the state of things indicated by Fig. 1. From this we may read off the conclusion,

$$D < A B C + a b c.$$

$$d < A B C + a b c.$$

Or, if Dora remain at home, her three sisters will be all at home or all out; and the same will be true if Dora goes out.

## PROBLEM II.

If  $A = B$  and  $B = C$ , what may be said of  $D$ ?

Impressing upon the machine our premises,

$$(A = B) = \left. \begin{matrix} A \prec B \\ B \prec A \end{matrix} \right\} = \left. \begin{matrix} A b \prec 0 \\ B a \prec 0 \end{matrix} \right\}$$

$$(B = C) = \left. \begin{matrix} B \prec C \\ C \prec B \end{matrix} \right\} = \left. \begin{matrix} B c \prec 0 \\ C b \prec 0 \end{matrix} \right\}$$

the same state of the logical universe is produced as by the premises of the preceding problem. Hence,

$$D \prec A B C + a b c.$$

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## XIX.

## ON THE CAPITALIZATION OF LAND IN EARLY SOCIETY.

BY DENMAN W. ROSS, PH. D.

Communicated January 13, 1886.

SEVERAL years ago, when I published my book upon the "Early History of Land-holding among the Germans,"\* I said, in my Preface, that I hoped before long to rewrite the book. I said this because I felt that the theory which I had to offer, while it explained the facts very well, did not, somehow, explain itself.

My theory was, to describe it very briefly, this: that the holding of land among the early Germans was a holding in common, but not a communistic holding; that the ownership of the land, in so far as there was any ownership of it, was vested, not in communities, but in individuals; that there was no such thing as ownership by communities. I believe that this theory sums up the facts correctly. I believe that it is a true theory; but it needs an explanation. The question may very well be raised, How did the ownership of the land come to be vested in individuals before the land was divided among them, while it was held in common? How, while the holding of the land was a holding in common, did it occur to individuals that they were proprietors? Is not a holding in severalties necessarily antecedent to the idea of individual proprietorship?

I believe that a holding of land in severalties is not necessarily antecedent to the idea of individual proprietorship; and I think that I can show you how, among our ancestors, the early Germans, individual proprietorship existed before — in many cases long before — there was any division of the land into severalties. Unless I am mistaken, individual proprietorship was, among the early Germans, the result, not of divisions of the land, but of what we may call capitalizations. Let me explain to you what I mean by this statement.

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\* Soule and Bugbee, Boston; Trübner & Co., London. 1883.

As long as there were plenty of wild animals, so that everybody could kill as many as he needed, — so that he could get plenty of meat to eat, and skins enough to clothe him, — there were no animals except wild animals. Animals were not domesticated; and property in animals — live stock — was unknown. But as the wild animals became scarce, some of the most tractable were caught and domesticated, and so converted into private property.

Up to this time the amount of land which the individual occupied was simply the land upon which he pitched his tent or built his hut; but after the introduction of property in animals, the amount of land which a man occupied depended mainly upon the number of his animals. If he had ten animals, he occupied land enough to support ten animals; if he had thirty animals, he occupied land enough for thirty animals. Every man turned all his animals out upon the land. It was a process of capitalizing the land. Every man had, in his animals, a certain amount of capital. This capital he invested in the land, and as a rule, he profited according to his investment.

The capitalists lived in companies, — companies of kinsmen; and the amount of land which each company capitalized depended upon the number of animals owned by its members. Each company occupied a pasture sufficient for the maintenance of all the animals belonging to its members. Then each member capitalized a certain number of shares, according to the number of his animals.

Suppose, for example, we have a company of four capitalists, — A, B, C, and D. Suppose A has six animals, B three, C two, and D four. Altogether they have fifteen. Allowing four acres of pasture for each animal, the company would require, for the fifteen animals owned by its members, sixty acres. Having, as a company, taken possession of sixty acres of pasture land, A would capitalize twenty-four ( $6 \times 4$ ) acres, B twelve ( $3 \times 4$ ), C eight ( $2 \times 4$ ), and D sixteen ( $4 \times 4$ ). The holding of land in this way may very properly be described as a holding of capitalized shares.

As long as there was plenty of live stock, and everybody had sufficient for his maintenance, it was not necessary to resort to agriculture. It was only among the poorer classes that agriculture was undertaken at first. There was plenty of land in the early time of which we are speaking, and everybody could cultivate as much as he pleased; but he never pleased to cultivate more than was absolutely necessary, — more than he could not help cultivating, — until he was able to make some of his fellow men do the work for him. Agriculture was very little resorted to until slavery, or serfdom, was introduced.

Before the introduction of servile labor, the freemen who were obliged to engage in agriculture capitalized certain amounts of the land by the application to it of their ploughs, their plough-oxen, and their seed. Just as soon, however, as men were obliged to resort to agriculture as a means of subsistence, they began to look about them for laborers to do the hard work which agriculture, especially primitive agriculture, necessitates. They began to appropriate laborers wherever they could lay hands upon them. Then we have property in laborers as well as in animals.

After the introduction of property in laborers, the amount of land which the freeman occupied, beyond his place of residence, depended, not only upon the number of his domesticated animals, but also upon the number of his enslaved laborers. If he had five laborers, he occupied as much land as the five laborers could cultivate; if he had ten laborers, he occupied as much land as the ten could cultivate. Thus the freemen began to capitalize shares of arable land according to the number of their laborers.

Of course, the amount of land which the laborer was able to cultivate depended upon the capital he had to work with. He could not do much work unless he was equipped with a plough, plough-oxen, and seed. The amount of land, therefore, which the freeman cultivated depended upon the number of his laborers who were equipped for service with ploughs, plough-oxen, and seed.

The capitalists continued, in most cases, to live together in companies; though it was not unusual for a large capitalist, the owner of many animals and many laborers, to settle by himself. The amount of land which a company of capitalists occupied depended upon the number of animals and equipped laborers owned by all the members together. Each company occupied a pasture sufficient for all the animals belonging to its members, and, in addition to that, as many lots of arable land as all the laborers belonging to the members could cultivate. Then each member of the company capitalized as many shares of the pasture land as he had animals, and as many lots of the arable land as he had laborers equipped for service with ploughs, plough-oxen, and seed. Suppose, for example, we have a company of four capitalists, — A, B, C, and D. Suppose A has five equipped laborers, B three, C eight, and D four. All together they have twenty equipped laborers. They occupy, as a company, twenty lots of arable land. Of these, A capitalizes five lots, B three, C eight, and D four. Again we have a holding of land in capitalized shares. It is arable land which is in this case capitalized.

The condition of things in early times was this: the land was unappropriated and undivided. It was free to all freemen. This being the case, every freeman turned his animals out to pasture, and every animal occupied its proportion of the land; and every season the freeman took as many lots of arable land as he had laborers equipped and able to cultivate them.

Wherever a tract of pasture land became fully stocked with animals, and there were no more arable lots for any more laborers, the freemen began to found colonies with the surplus of their animals and laborers. The holding of land was the same, however, in the colonies as in the original settlements. The freemen took shares in the colonies according to the number of laborers and animals contributed by each one.

Sometimes the freemen who had large numbers of laborers and animals left the company of other freemen and settled by themselves; but these isolated settlements soon became family settlements, because, when the first settler died, his sons took his animals and his laborers and divided them; and after that each man held, not a separate portion of land, but certain capitalized shares, according to the number of his animals and his laborers.

In time, however, the land became everywhere thickly settled, and there was no more room anywhere, either for animals or for laborers. All the land was capitalized. Then one of two things happened. Either the land was divided into severalties, representing the previously existing capitalized shares, or else the capitalized shares were counted, defined, and converted into undivided properties of the persons who had capitalized them.

Between different families the land was generally divided into severalties; but between the members of a family it was more customary to count, define, and distribute the existing capitalized shares, and then to hold them in common, each man holding as many undivided shares of the land as he had previously capitalized. If, for example, A had capitalized twenty shares of arable land, B thirty, C fifteen, and D twelve, the number of shares of arable land was fixed at seventy-seven ( $20 + 30 + 15 + 12 = 77$ ); and A became proprietor of twenty shares, B proprietor of thirty, C of fifteen, and D of twelve. They did not, however, divide the land according to their several shares, but they held the shares in common. The pasture land was held in the same way, — in undivided shares. If A had turned sixty animals out to pasture, capitalizing sixty shares of the pasture, and if B had similarly capitalized thirty shares, C forty, and D fifteen, the number of

capitalized shares was fixed at one hundred and forty-five ( $60 + 30 + 40 + 15 = 145$ ); and of these shares A became proprietor of sixty, B proprietor of thirty, C of forty, and D of fifteen. But the shares were not divided. They were held in common. A and his descendants held land enough for sixty animals in the common pasture. They could turn out sixty animals, but no more than sixty. B and his descendants were limited to thirty animals, D and his descendants were limited to forty, C and his descendants to fifteen. So long as the pasture remained undivided, rights of property were represented by rights of common. These rights were very strictly defined according to what they represented.

The associate proprietors had each his dwelling-place, — his house, with sheds, yards, and generally an enclosed garden. He had also houses, with sheds, yards, and gardens for his laborers. So much property the proprietors held in severalties; but the shares of arable land and of pasture land were generally held in common, in the manner described. At the same time, the undivided shares of arable and pasture land were just as much the property of the different proprietors as the dwelling-places which they held in severalties. They were inherited from the very first moment of their existence, and, with the consent of the heirs, they were alienable. The capital, consisting of animals and laborers, which was put into the land, was hereditary and alienable; consequently the capitalized shares of land were hereditary and alienable also. No doubt appears to have been held upon this point among the early Germans.

It was in this way that individuals became proprietors of the land before the land was divided into severalties; and we see clearly enough how a division of the land into severalties is not necessarily antecedent to the idea of individual proprietorship. The German freemen were at first simply capitalists capitalizing shares of the land according to their means. The rich men, who had many animals and laborers, capitalized a great many shares of the land; the poor men, who had only a few animals and a few laborers, capitalized only a few shares. Then, as the land became thickly settled and completely capitalized, the existing capitalized shares were counted, defined, and distributed among the capitalists; and the capitalists became in this way proprietors of undivided shares of the land. Each one became proprietor of the shares he had capitalized. The undivided properties thus established were hereditary and alienable (with the consent of the heirs), together with the capital put upon them. When a man died leaving four sons, and property amounting to twelve equipped laborers

and twelve shares of arable land, each son took three laborers and three shares of the land. If the father left sixty animals and sixty shares of the pasture land, each son took fifteen animals and fifteen shares of the pasture,—that is to say, pasture for fifteen animals. With the consent and approval of his sons, the deceased might, during his lifetime, have alienated some of his laborers and shares of arable land, and some of his animals and shares of pasture land. The early records are full of illustrations and proofs for these statements. As I have given numerous extracts and references in my book, I will not repeat them here. The evidence of the early records leads us to this conclusion: that individual proprietorship of land was among the early Germans, in almost all cases, antecedent to the division of the land into permanent severalties; that the earliest form of proprietorship was a proprietorship of what may be called capitalized shares.

As time went on, the undivided shares of arable land were, first here and there, then almost everywhere, converted into severalties. Then we have private holdings instead of undivided ones, private property instead of undivided property.

The disposition of these severalty holdings of arable land depended mainly upon the configuration and character of the soil. In mountainous, hilly, and especially in rocky countries, where the good arable land lay scattered here and there in small tracts, it was necessary for the proprietors—for their laborers at any rate—to distribute themselves in isolated farmsteads in the neighborhood of the isolated fields which they were to cultivate. Under such conditions, we have what the German writers call the *Einzelhof-system*. In valleys and in flat regions generally, where the arable land lies in large tracts, it was customary to have the dwelling-places—at least those of the laborers who were to cultivate the land—close together in villages, and the lots of arable land in long strips side by side, or radiating from a common centre. Vestiges of this arrangement of the lots may still be observed in certain places. The arrangement is a very convenient and satisfactory one, except in cases where the strips of arable land are not equally fertile and productive. It was very important, in the times of which we are writing, that the arable lots should be equally productive, because each one of the laborers who cultivated the lots paid a certain amount of produce to his master, and the amount was fixed by tradition or local custom, without regard to the land from which the produce was to be obtained. It was necessary therefore, in justice, that the lots of land should be, as far as possible, equally productive. From the proprietor's point of view, also, it was important

that the lots should be of equal value. When property has been held in undivided shares, and a division has to be made, it is necessary, in justice, that the unit shares of the division should be of equal value. The primitive custom was to lay out as many equal lots as there were unit shares to be distributed. Then the proprietors, or their representatives, took possession, each one, of as many lots as were due to him. There was a rush for the best, and the strongest men got them. Then it was proposed to draw lots, and to distribute the lots of land accordingly. This method, while it prevented quarrelling, did not secure justice. Next, it was proposed that the lots of land should be held in rotation. He who held the first lot one year was the next year to take the second lot, then the third, and so on, until he had taken all the lots, one after another; then he took the first one again. This plan was adopted in many places. Still another plan, very often adopted, was to divide the arable land by sections (*Gewannen*), each section equally fertile in all parts, and to assign to each unit share an equal portion of every section. Suppose I have a tract of land to divide into three equal shares, and half of the tract is not very good. I separate the good half from the poor half, and divide each half into three equal parts. Then I assign one third part of each half to a share. This illustrates the principle upon which the arable land was divided into equal shares by sections. In other cases the shareholders measured off as many acre lots as there were unit shares to be distributed, and assigned one acre lot to each share; then measured off another set of acres, and distributed them in the same way; then another set, and another, until all the arable land was distributed in acre lots in equal sections (*Gewannen* again) of a large open field. This was a very common mode of dividing the land. Vestiges of all these different modes of dividing the land may be seen, even to-day, in certain parts of Germany, of France, and of England.

Where the same land was cultivated year after year, it lost its vitality, and became less and less productive. This fact was observed, and it became customary to allow the land which was cultivated in one year to lie fallow the next year, or at least once in three years. Where the arable lots were isolated one from the other, and also where they lay in strips, side by side, every cultivator could divide his land into two or three fields as he pleased. He could arrange a system of rotation to suit himself; but in cases where the arable lots were intermixed in sections (*Gewannen*), it was necessary to adopt a system of rotation by which all the cultivators would be bound. The system generally adopted was to divide the open field into two or

three fields, usually three. Then one of these fields lay fallow every other year where there were two of them, or once in three years where there were three of them.

The intermixture of properties which I have just described made it necessary for the proprietors to carry on the processes of agriculture simultaneously, and more or less co-operatively. It was necessary for the proprietors, or their representatives, to meet and agree upon certain courses of action. It was also necessary to appoint officers to represent the meetings, and to see that everybody acted according to agreement. This was the beginning of systematic local self-government upon democratic principles; for the most remarkable feature connected with the organization of these local governments was the very general adoption of the principle of equal suffrage, without regard to inequalities of property. Every proprietor had an equal voice in the making of rules and regulations for his village or town, and in appointing officers and magistrates to see that they were observed. Every proprietor had an equal voice in these matters without regard to the extent of his property. He who owned one share of the land had just as much influence in the town meeting as he who owned five shares or ten. On the one hand we have inequalities of property, and on the other hand equal rights of suffrage, — unequal property rights with equal political rights, — just as it is among ourselves to-day.

As time went on, some of the proprietors ceased to be proprietors; but as long as they continued to reside in their town, they attended the town meetings, and exerted an influence in them. The result was, that the rights of proprietors were often curtailed for the accommodation and satisfaction of the non-proprietors. The non-proprietors, for example, wanted the right to turn their animals out upon the pasture land of the town, which was the property of the proprietors, which was owned by the proprietors in undivided shares; or else they wanted to have the privilege of turning their animals out upon the stubble of the arable fields after the harvest had been gathered in. In many cases the non-proprietors were so numerous in the town meeting, or their appeals were so forcible, that they were able to obtain rights in the land which did not properly belong to them as non-proprietors. Without being proprietors, they obtained rights amounting to rights of property. In some cases, indeed, they succeeded in having the pasture land of the town, including the forest and waste, defined as the common property of all the townsmen, including the non-proprietors.

This is, very briefly, without going into details, the history of the agricultural communities of the Middle Ages, in so far as these communities were from the first communities of freemen. We must not forget, however, that most of the mediæval communities were originally colonies of laborers, slaves or serfs, — simply capital put upon the land by the freemen for their profit. The colonies of slaves or serfs were put under the charge of agents, who took care of them, just as in our own time the superintendents of factories take charge of the factories for their employers, and collect the produce for their benefit.

Wherever the rule of indivisible estates was adopted, as it was in many places, the colonies of serfs remained undivided. Under the system of inheritance by primogeniture, the colonies passed to successions of individuals. Under the feudal system, they were distributed among the feudal lords and their vassals. Some of them remained in the domain of the lord; others were given out as benefices.

As time went on, the serfs were emancipated, and we have, instead of colonies of serfs, colonies of freemen, — free tenants of the land. The serfs who became freemen began very soon to act as freemen. They began to hold meetings; they began to make rules and regulations regarding the conduct of local affairs; they began to appoint officers and magistrates to represent them, and to carry out their resolutions, — to see that their rules and regulations were obeyed. Again, local governments were established upon democratic principles. The history of the serf colonies, from this time on, is only a repetition of the history of the proprietary villages or towns already described. On the one hand, we have equal suffrage in the town meeting; on the other hand, unequal holdings of town land. Then we have townsmen who have no holdings of town land, who nevertheless attend the town meetings and exert an influence therein. Then we have an effort on the part of the non-holders of land to obtain rights which belong properly only to those who are holders. In some cases, the efforts of the non-holders were so successful that they were able to have the pasture land, including the forest or waste, defined as the common property of all the townsmen, including the non-holders of land.

With the overthrow of the feudal system the communities of free tenants, originally colonies of serfs, became communities of proprietors. As such, they are undistinguishable from the communities of proprietors first described, which were free and independent from the beginning.

In conclusion, it is hardly necessary for me to remind you, that a holding of land in capitalized shares cannot be properly described as a communistic holding. The holding of land among the early Germans was in no respect communistic.

Cæsar tells us, and it is no doubt true, that the German freeman had at first no separate or private property in the land, no defined or limited share of it; but we cannot infer from this statement any equality of rights in the land. There was plenty of land — more than enough for everybody — at that time; so there was no *raison d'être* for any rights in it, equal or unequal. The question is, not what rights men had in the land, but how they occupied it, how they made it productive. Cæsar tells us that there were among the Germans rich men and poor men. At the same time he tells us that wealth consisted chiefly of cattle, — live stock. Of course, the animals must have been turned out upon the land to pasture. The rich men turned out many, the poor men a few. They profited accordingly; the rich men grew richer fast, the poor men slowly. Agriculture was not much resorted to in the time of Cæsar, nor in the time of Tacitus, by freemen. Tacitus tells us, in his *Germania*, that the freemen avoided agricultural labor as much as possible. They spent most of their time in eating, drinking, and sleeping, in hunting and other amusements, and in fighting with their neighbors. Feeble old men and the women looked after the household and the cultivation of the land. They had slaves or serfs, who took charge of the cattle and labored in the fields. In the very next paragraph, after describing the condition of these slaves or serfs, Tacitus says that arable lots (*agri*) were occupied according to the number of cultivators (*pro numero cultorum*). Shall we not infer that the cultivators who took the arable lots were the slaves or serfs? The slaves or serfs must at any rate be counted among them; and we can infer that the freeman who had ten serfs took ten lots of arable land, while he who had only five serfs took only half as many. This inference, which seems very fairly indicated by the words of Tacitus, is sustained by the concurrent testimony of the later records, — laws, formulas, and documents. The mode of taking up shares of arable land according to the number of cultivators corresponds with the mode of taking up shares of pasture land according to the number of animals. We find no end of examples and illustrations of these practices in the later records. As I have given innumerable extracts and references to establish this statement in my book, already referred to, I need not repeat them.

I wish now to call your attention to the applicability of the phrase

*holding land in capitalized shares* to the condition of things which I have described. The phrase occurred to me not long ago, and it seemed to me worthy of your consideration. Suppose we stop talking about a primitive communism in respect to land. Suppose, also, we stop talking about a primitive proprietorship. Instead of using these phrases, neither of which has any applicability to the state of things described in the earliest records, let us talk of the *capitalization of the land*, and of the *holding of the land in capitalized shares*. Upon these phrases, I think, both the advocates of a primitive communism and the advocates of a primitive proprietorship may be induced to unite and agree. After all, the disagreement between the advocates of the two opposed theories is very largely a disagreement in the use of terms.

## XX.

## OBSERVATIONS OF VARIABLE STARS IN 1885.

BY EDWARD C. PICKERING.

Communicated February 10, 1886.

THE present publication is the third in a series of annual statements relating to variable stars, which was begun in 1884. The value of these statements mainly depends upon their completeness, and it is therefore to be hoped that all observers of variable stars will send accounts of their work to the Observatory of Harvard College as soon as possible after the close of each year. The principal facts desired are the designations of the stars observed, and the number of nights on which each of them was examined. But brief statements of the results obtained, such as the times of maxima and minima, are also desirable, when they can be readily furnished. Information with regard to the instruments employed and the method of observation will likewise be very serviceable.

The evident need of a new catalogue of variable stars has occasioned some preparations for such a list to be made, and the question of publishing it in the *Astronomische Nachrichten* has been discussed by correspondence with Dr. Krüger, the editor of that periodical. It is, however, desirable that the catalogue, when published, should have a definite and authoritative character, so that it appears best to avoid premature action with regard to it. Meanwhile, it has been decided to make no addition to the list of known variables published in the article entitled "Recent Observations of Variable Stars," although some stars not belonging to that list are now certainly known to be variable. In the present publication such stars are therefore still mentioned in connection with suspected variables. Several stars included in the original list are not there designated by the letters which have at times been applied to them, and it has been decided not to make any change in this respect for the present, in order to avoid the possibility of confusion. Observers are therefore requested to give the right ascensions and declinations of all stars mentioned in their statements, unless they can be designated by the numbers given in the first columns of Tables I. and II. in "Recent Observations of Variable Stars."

Photometric observations of all the stars with which variables are known to have been compared have been undertaken at the Observatory of Harvard College, to which all observers are requested to send lists of the comparison stars employed by them, or references to the published places of such stars. The lists of Argelander, Schönfeld, and Oudemans form the foundation of the work, but information of many comparison stars not included in those lists has been received, and these stars are also to be observed.

It is hoped that it will ultimately be practicable to give the number of observations of each variable star which have been made each year since its discovery. Any information of this kind, hitherto unpublished, will therefore be gratefully received.

It is much to be desired that observers stationed in the southern hemisphere should pay some attention to the variable stars which their situation gives them special facilities for observing, and should send some notice of their work for appearance in this series of publications. It will be seen on examination that no variables in large southern declinations are known to have been recently observed.

The present report relates principally to observations made during 1885; but earlier observations, notice of which has been received since the last report was published, are also mentioned in it. The observers whose work is here stated are named below in alphabetical order, with the abbreviations employed to designate them in the subsequent tabular statements.

B. These observations were made by Mr. T. W. Backhouse, of Sunderland, England, where most of the comparisons were made. A refracting telescope by Cooke, aperture  $4\frac{1}{4}$  inches, magnifying powers 38 and 75, was often used; other observations were made with the finder, power 9, and the rest with a field-glass and similar instruments of low power, or with the naked eye. The methods of comparison were chiefly three: that of Argelander, that in which the relative brightness of the star observed is indicated by a fraction of the apparent difference between two comparison stars, and that of verbal description, in which, however, the words employed are regarded as having numerical values. A copy of the observations has been sent to the Observatory of Harvard College.

D. These observations were made by Dr. N. C. Dunér, at the Observatory of Lund, Sweden, according to the method of Argelander.

Ee. These observations were made by Mr. John H. Eadie, at Bayonne, New Jersey. The telescope employed was made by John Byrne; its aperture is  $3\frac{1}{4}$  inches, and the lowest magnifying power

about 50. Argelander's method of comparison is used. A copy of the observations has been furnished to the Harvard College Observatory. Mr. Eadie acts in co-operation with Mr. Parkhurst in a manner which is explained in the remarks upon Mr. Parkhurst's observations. This system of co-operation appears to be highly efficient and economical. It deserves extension and general introduction among observers not too far separated for ready communication with each other.

En. These observations were made by the Rev. T. E. Espin, of Walsingham, Darlington, England. The instruments employed were a binocular glass and reflecting telescopes of 9 and  $17\frac{1}{4}$  inches in aperture, the last by Calver.

G. These observations were made by Mr. J. E. Gore, of Ballysodare, Ireland, by Argelander's method. The instrument was a binocular field-glass having object-glasses of 2 inches in aperture, and a magnifying power of about six diameters.

Hg. These observations were made at Dorpat, by Dr. E. Hartwig.

Hn. These observations were made by the Rev. J. Hagen, S. J., at the College of the Sacred Heart, Prairie du Chien, Wisconsin. The instrument is a telescope by Merz; its aperture is 3 inches. The observations were made by the division into tenths of the interval between two comparison stars. A copy of the observations has been furnished to the Harvard College Observatory. Mr. Zaiser has taken part in the work as an assistant.

K. These observations were made by Mr. George Knott, at Knowles Lodge, Cuckfield, Hayward's Heath, England. The telescope employed was made by Alvan Clark and Sons; its aperture is  $7\frac{1}{2}$  inches, and that of the finder 2 inches. The variable is compared with stars differing little from it in brightness; the magnitudes of the comparison stars, and sometimes the magnitude of the variable, are determined by the method of limiting apertures.

M. These observations, which relate exclusively to suspected variables, were made with the meridian photometer of the Harvard College Observatory. The observers using this instrument are E. C. Pickering and O. C. Wendell. The magnitudes of the stars observed with it are referred to a series of one hundred circumpolar stars, the brightness of which was determined by observations described in Volume XIV. of the Annals of the Observatory.

P. These observations were made by Mr. H. M. Parkhurst, at Brooklyn, N. Y. The instrument is a telescope made by Fitz; its aperture is 9 inches, and the magnifying powers employed are 56 and 150. Many of the observations are made by Argelander's method,

and others by photometric apparatus devised by Mr. Parkhurst, and partially described in the article entitled "Recent Observations of Variable Stars," which was mentioned above. A copy of the observations has been furnished to the Harvard College Observatory. The co-operation of Mr. Eadie with Mr. Parkhurst has already been mentioned. The former observer undertakes the observation of certain stars while they are sufficiently bright to be well seen in his telescope, and when they become too faint for further observations he notifies Mr. Parkhurst to begin observing them. When they are again sufficiently bright to be observed by Mr. Eadie, he is informed of the fact by Mr. Parkhurst. This system permits each observer to employ his time to the best advantage. It is hoped that some astronomer having a large telescope at command will undertake observations of the stars studied by Messrs. Parkhurst and Eadie at times when they are too faint to be followed by either observer.

**Sk.** Professor Safarik, of Prague, Austria, has furnished a statement of observations made by him in 1885, and also of those made in 1883 and 1884, which were incompletely noticed in the circular published in 1885. The observations were made by Argelander's method. The instrument used previous to March, 1885, was a Newtonian reflector  $6\frac{1}{2}$  inches in aperture, with a mirror of silvered glass. The ordinary magnifying power was 32. The finder had an aperture of 3 inches, and a magnifying power of 12. Subsequent observations were made with a refractor by Schröder, with an aperture of 4.5 inches, a magnifying power of 23, and a field of  $1^{\circ} 30'$ . Between 1880, January 1, and 1884, December 31, Professor Safarik has made a little more than 5700 observations of about 100 stars. During the year 1885 he made 1647 observations of 89 stars. On all suitable occasions he estimates the colors of the stars observed upon Schmidt's scale. The number of observations made in the separate months of each year are given in the statements just described.

**Sr.** These observations were made, according to Argelander's method, by Mr. E. F. Sawyer, at Cambridgeport, Massachusetts, by means of an opera-glass for the brighter stars, and of a field-glass for the others.

**Zr.** The observations of Assistant Zaiser have already been mentioned under the heading **Hn**.

Table I. indicates the progress of observation for stars included in Table I. of previous reports. Other stars, whether known or suspected to be variable, are included in Table II. All the columns of Table I. except the last are repeated from the statement of the previous year.

The first column of the left-hand page gives a provisional number for designating the star. This number is taken from Schönfeld's Catalogue when the star occurs there; in other cases, a letter is added to the number. The second column contains numbers from the Photometric Catalogue called Harvard Photometry, and published in Volume XIV. of the Annals of the Harvard College Observatory. The following columns contain the usual designation of the star, its right ascension and declination for 1875, magnitude at maximum and minimum, and period in days.

The first column of the right-hand page repeats the number to be used for the provisional designation of the star. The second gives the class to which the star belongs, upon the system of classification employed in the Proceedings of the American Academy of Arts and Sciences, XVI. 257. Upon this system, Class I. includes temporary stars; Class II., stars undergoing large variations in periods of several months; Class III., irregularly variable stars, undergoing but slight changes in brightness; Class IV., variable stars of short period, like  $\beta$  *Lyræ* or  $\delta$  *Cephei*; Class V., Algol stars, or those which at regular intervals undergo sudden diminutions of light, lasting for a few hours only. The third column gives the name of the discoverer, and the fourth column the date.

The last column contains the number of nights on which each star was observed by the astronomer whose designation is attached to the number. The abbreviations employed have been explained above. The designation Sk. is preceded by three numbers, which relate respectively to observations made in 1883, 1884, and 1885. A dash replaces a number when some observations are known to have been made, but their number has not been ascertained.

Table I. is followed by a series of remarks containing observed dates of maximum and minimum, and other information derived from the observers with regard to particular stars.

Table II. indicates the progress of observation of stars suspected or known to be variable, but not included in Table I. for reasons previously explained. The stars are designated in the first column by Mr. Chandler's provisional numbers, as in the previous statement. The number is replaced by a dash when the star has not yet been entered in Mr. Chandler's catalogue. The second and third columns give the right ascensions and declinations of the stars for 1875. The fourth column gives the number of observations made by each observer, as in the last column of Table I. The abbreviations are likewise the same. The letters in the last column refer to the remarks on page 334.

TABLE I. — VARIABLE STARS.

No.	H.P.	Name.	R. A. 1875.	Dec. 1875.	Max.	Min.	Per.
			h. m. s.	° ' "	m.	m.	d.
0a	—	Ceti	0 15 26	-20 45.1	5.2	7.0	—
1	51	T Cassiopeiae	16 29	+55 5.9	6.5—7.0	11—11.2	436
2	54	R Andromedae	17 28	+37 53.0	5.6—8.6	<12.8	404.7
3	—	S Ceti	17 42	-10 1.3	7.0—8.0	<10.7	323.6
4	—	B Cassiopeiae	17 52	+63 27.2	>1	?	—
5	—	T Piscium	25 31	+13 54.6	9.5—10.2	10.5—11.0	Irr.
6	94	a Cassiopeiae	33 25	+55 51.1	2.2	2.8	Irr.
6a	—	U Cephei	51 18	+81 12.1	7.0	9.5	2.5
7	—	S Cassiopeiae	1 10 30	+71 57.2	6.7—8.5	<13	615
8	—	S Piscium	11 2	+ 8 16.3	8.8—9.3	<13	406.6
8a	—	Piscium	16 22	+12 12.7	10	14	—
8b	—	Ceti	19 31	- 4 34.6	6.5	7.8	—
8c	—	R Sculptoris	21 13	-33 11.5	5½	7½	207
9	—	R Piscium	24 12	+ 2 14.1	7.4—8.3	<12.5	345
10	—	S Arietis	57 55	+11 55.5	9.1—9.8	<13	288.8
11	—	R Arietis	2 9 1	+24 28.4	7.6—8.5	11.9—12.7	186.2
12	370	o Ceti	13 1	- 3 32.7	1.7—5.0	8—9	331.3
13	—	S Persei	13 54	+58 0.8	8.5?	<9.7	—
14	—	R Ceti	19 39	- 0 44.6	7.9—8.7	<12.8	167.1
15	—	T Arietis	41 22	+16 59.3	7.9—8.2	9.4—9.7	324
16	489	p Persei	57 10	+38 21.3	3.4	4.2	Irr.
17	496	β Persei	3 0 2	+40 28.4	2.2	3.7	2.9
18	—	R Persei	22 6	+35 14.3	8.1—9.2	12.5	208.8
19	657	λ Tauri	53 45	+12 8.2	3.4	4.2	4.0
20	—	T Tauri	4 14 43	+19 14.3	9.2—11.5	12.8—	Irr.
21	—	R Tauri	21 27	+ 9 52.9	7.4—9.0	<13	325.6
22	—	S Tauri	22 22	+ 9 40.1	9.9	<13	378
22a	—	Doradus	35 19	-62 19.4	5½	6½	—
23	—	V Tauri	44 48	+17 19.6	8.3—9.0	<12.8	168.6
24	—	R Orionis	52 13	+ 7 56.3	8.7—8.9	<13	378.8
25	877	ε Aurigæ	53 0	+43 38.2	3.0	4.5	Irr.
26	880	R Leporis	53 55	-14 59.7	6—7	8.5?	437.8
27	—	R Aurigæ	5 7 12	+53 26.6	6.5—7.4	12.5—12.7	465
27a	—	S Aurigæ	18 52	+31 2.3	9.4	<13	—
28	—	S Orionis	22 50	- 4 47.5	8.3?	<12.3	—
29	1005	δ Orionis	25 37	- 0 23.6	2.2?	2.7	Irr.
29a	—	Orionis	29 42	- 5 33.5	10	13	—
30	1091	α Orionis	48 24	+ 7 23.3	1	1.4	Irr.
31	1160	η Geminorum	6 7 20	+22 22.4	3.2	3.7—4.2	229.1
31a	—	Monocerotis	16 26	- 2 8.1	7	<10	—
32	1205	T Monocerotis	18 29	+ 7 9.1	6.2	7.6	26.8
33	—	R Monocerotis	32 21	+ 8 50.7	9.5	11.5	Irr.
34	1256	S Monocerotis	34 6	+10 0.5	4.9	5.4	3.4
35	—	R Lyncis	50 59	+55 30.2	9?	<12.3	—
36	1334	ζ Geminorum	56 41	+20 45.1	3.7	4.5	10.2
37	—	R Geminorum	59 49	+22 53.8	6.6—7.3	<12.3	371.0
38	—	R Canis min.	7 1 50	+10 13.1	7.2—7.9	9.5—10.0	335.0
38a	—	Puppis	9 43	-44 26.2	3½	<6	135
38b	—	V Geminorum	16 10	+13 21.8	8.5	12—13½	276
38c	1417	U Monocerotis	24 50	- 9 31.0	6.0	7.2	46.0
39	—	S Canis min.	25 56	+ 8 35.0	7.2—8.0	<11	332.2
40	—	T Canis min.	27 3	+12 0.6	9.1—9.7	<13	335.2
40a	—	Canis min.	34 34	+ 8 40.2	8½	13.5	405

TABLE I.—VARIABLE STARS.

No.	Class.	Discoverer.	Date.	Observations, 1885.
0a	—	Chandler	1881	1 G. 30 Sr.
1	II.	Krüger	1870	6 Ee. 1 En. 3 G. 24,42,27 Sk.
2	II.	Argelander	1858	3 D. 2 Ee. 5 P. 15,19,8 Sk. 27 Sr.
3	II.	Borelly	1872	3 Ee. 7 P. 9,0,0 Sk.
4	I.	Tycho Brahe	1572	—
5	II.	Luther	1855	4 Ee. 1 P.
6	III.	Birt	1831	2 B. 32 Sr.
6a	V.	Ceraski	1880	21 Hn. 3 K.
7	II.	Argelander	1861	8 P. 67,39,23 Sk.
8	II.	Hind	1851	10 Ee. 4 P. 1,0,0 Sk.
8a	—	Peters	1880	11 P.
8b	—	Gould	1874?	1 Hn. 11 Sr.
8c	II.	Gould	1872?	—
9	II.	Hind	1850	12 P. 11,2,0 Sk.
10	II.	Peters	1865	10 P.
11	II.	Argelander	1857	6 Hn. 10 P. 7,6,0 Sk.
12	II.	Fabricius	1596	35 B. 37 G. - Hg. 15 K. 18,23,17 Sk. 54 Sr.
13	II.	Krüger	1873	- Hg. 21 Hn. 43,39,53 Sk.
14	II.	Argelander	1866	11 P. 9,6,8 Sk.
15	II.	Auwers	1870	12 Hn. 37,30,16 Sk
16	II.?	Schmidt	1854	36 Sr.
17	V.	Montanari	1669	10 B. 3 Hg. 1 Sr.
18	II.	Schönfeld	1861	6 Ee. 12 H. 6 P. 8,14,9 Sk
19	V.	Baxendell	1848	9 Zr.
20	—	Hind	1861	3 K. 8 P. 5,5,3 Sk.
21	II.	Hind	1849	6 Ee. 9 P. 19,9,5 Sk.
22	II.	Oudemans	1855	6 Ee. 9 P. 19,9,6 Sk.
22a	—	Gould	1874?	—
23	II.	Auwers	1871	12 P. 15,8,7 Sk.
24	II.	Hind	1848	2 Ee. 4,1,0 Sk.
25	III.	Fritsch	1821	34 Sr.
26	II.	Schmidt	1855	17,11,10 Sk. 21 Sr.
27	II.	At Bonn	1862	12 Hn. 3 P. 11,19,0 Sk.
27a	II.	Dunér	1881	21 D. 5 P.
28	II.	Webb	1870	13 Ee. 1 K. 10 P. 25,19,23 Sk.
29	III.	J. Herschel	1834	14 Sr.
29a	—	Bond	1863	11 Ee. 10 P.
30	III.	J. Herschel	1836	9 Zr.
31	II.?	Schmidt	1866	2 B. 20 Sr.
31a	—	Schönfeld	1883	13 Sr.
32	IV.	Gould	1871	71 Sr.
33	II.	Schmidt	1861	—
34	IV.	Winnecke	1867	29 Sr.
35	II.	Krüger	1874	11 P. 5,21,15 Sk.
36	IV.	Schmidt	1844	22 Sr. 10 Zr.
37	II.	Hind	1848	6 K. 11 P. 0,0,7 Sk.
38	II.	At Bonn	1854	8 Hn. 0,14,23 Sk.
38a	II.	Gould	1872	—
38b	II.	Baxendell	1880	1 Ee. 6 K.
38c	II.?	Gould	1873	20 En. 64 Sr.
39	II.	Hind	1856	2 Ee. 7 K. 0,14,25 Sk.
40	II.	Schönfeld	1865	1 Ee.
40a	II.	Baxendell	1879	2 Ee. 2 K.

TABLE I. — *Continued.*

No.	H.P.	Name.	R. A. 1875.	Dec. 1875.	Max.	Min.	Per.
			<i>h. m. s.</i>	<i>° ' "</i>	<i>m.</i>	<i>m.</i>	<i>d.</i>
41	—	S Geminorum	7 35 32	+23 44.6	8.2—8.7	<13	294.2
42	—	T Geminorum	41 48	+24 2.7	8.1—8.7	<13	288.1
42a	—	S Puppis	43 6	—47 8.3	7½	9	—
43	—	U Geminorum	47 41	+22 19.7	8.9—9.7	13.1	Irr.
43a	—	Puppis	55 0	—12 32	8½	<14	310
44	—	R Cancri	8 9 40	+12 6.5	6.2—8.3	<11.7	354.4
45	—	V Cancri	14 36	+17 40.9	6.8—7.2	<12	272
46	—	U Cancri	28 37	+19 19.5	8.2—10.4	<13	305.7
47	—	S Cancri	36 48	+19 29.0	8.2	9.8	9.5
48	—	S Hydræ	47 3	+3 32.4	7.5—8.5	<12.2	256.4
49	—	T Cancri	49 32	+20 19.7	8.2—8.5	9.3—10.5	484.2
50	—	T Hydræ	49 35	—8 39.8	7.0—8.1	<12.5	289.4
50a	—	R Carinæ	9 29 6	—62 14.2	4.4	9.3	313
51	—	R Leonis min.	38 4	+35 5.2	6.1—7.5	<11.0	374.7
52	1752	R Leonis	40 50	+12 0.5	5.2—6.4	9.4—10.0	312.6
52a	—	l Carinæ	41 49	—61 55.9	3.7	5.2	31.2
52b	—	Leonis	53 3	+21 51.6	8½	8.6<13	280½
52c	—	Antliæ	10 4 22	—37 7.1	6½	<8	—
52d	—	Carinæ	5 23	—60 56.3	6½	—	—
52e	—	U Leonis	17 21	+14 38.1	9½	Inv.	—
52f	1869	Hydræ	31 22	—12 44.1	4½	6	—
53	1880	R Ursæ maj.	35 47	+69 25.9	6.0—8.1	12	303.4
54	—	η Argus	40 13	—59 1.6	>1	6.3	Irr.
54a	—	T Carinæ	50 18	—59 51.2	6.2	6.9	—
55	—	R Crateris	54 25	—17 39.2	>8	<9	—
56	—	S Leonis	11 4 23	+6 8.5	9.0—9.7	<13	187.6
57	—	T Leonis	32 2	+4 3.9	10?	<13	—
58	—	X Virginis	55 27	+9 46.1	7.8?	<10	—
59	—	R Comæ	57 51	+19 28.8	7.4—8.0	<13	363
60	—	T Virginis	12 8 12	—5 20.4	8.0—8.8	<13	337
61	—	R Corvi	13 10	—18 33.5	6.8—7.3	<11.5	318.6
61a	—	— Virginis	27 26	—3 43.8	8	14	210±
62	—	T Ursæ maj.	30 42	+60 10.6	7.0—8.3	12.2	255.6
63	2147	R Virginis	32 10	+7 40.6	6.5—7.5	10.0—10.9	145.7
63a	—	R Muscæ	34 28	—68 43.3	6.6	7.3	0.9
64	—	S Ursæ maj.	38 28	+61 46.7	7.7—8.2	10.2—11.1	224.8
65	—	U Virginis	44 46	+6 14.0	7.7—8.1	12.2—12.8	207.4
66	—	W Virginis	13 19 35	—2 43.4	8.7—9.2	9.8—10.4	17.3
67	—	V Virginis	21 21	—2 31.4	8.0—9.0	<18	251
68	2275	R Hydræ	22 53	—22 38.0	4.0—5.5	10?	469.3
69	2289	S Virginis	26 29	—6 33.0	5.7—7.8	12.5	374.0
69a	—	Virginis	14 3 37	—12 42.7	9	14	—
69b	—	R Centauri	7 35	—59 19.8	6	10	—
70	—	T Bootis	8 14	+19 39.1	9.7?	<13	—
71	—	S Bootis	18 41	+54 22.7	8.1—8.5	13.2	272.4
72	—	R Camelopardi	27 8	+84 23.8	7.9—8.6	12?	266.2
73	2445	R Bootis	31 41	+27 16.9	5.9—7.5	11.3—12.2	223.0
73a	2459	Bootis	37 56	+27 3.6	5.2	6.1	370?
73b	—	Bootis	48 33	+18 12.1	9.1	12.0—13.6	173.8
74	2506	δ Libræ	54 18	—8 1.2	4.9	6.1	2.3
74a	—	Libræ	15 3 37	—19 33.9	10	<13.5	700±
74b	—	R Triang. Austr.	8 37	—66 2.1	6.6	8.0	3.4
75	—	U Coronæ	13 6	+32 6.4	7.6	8.8	3.5
76	—	S Libræ	14 13	—19 56.1	8.0	12.5?	—
77	—	S Serpentis	15 48	+14 45.9	7.6—8.6	12.5?	361.0

TABLE I. — *Continued.*

No.	Class.	Discoverer.	Date.	Observations, 1885.
41	II.	Hind	1848	—, —, 29 Sk.
42	II.	Hind	1848	—, —, 31 Sk.
42a	—	Gould	1874?	—
43	II.?	Hind	1855	2 Hg. 45 K. 49,54,54 Sk.
43a	II.	Pickering	1881	—
44	II.	Schmidt	1829	1 Ee.
45	II.	Auwers	1870	7 P. 8,6,0 Sk.
46	II.	Chacornac	1853	1 Ee. 3 Hn. 6 K. 16,17,8 Sk.
47	V.	Hind	1848	1 Ee. 32 Hn. 2 K.
48	II.	Hind	1848	5,1,22 Sk. 22 Sr.
49	II.	Hind	1850	1 En. 4 P. 6,5,12 Sk.
50	II.	Hind	1851	4,12,3 Sk.
50a	II.	Gould	1871	—
51	II.	Schönfeld	1863	2 P. 24 Sr.
52	II.	Koch	1782	72,34,31 Sk. 38 Sr.
52a	—	Gould	1871	—
52b	II.	Becker	1882	—
52c	—	Gould	1872	—
52d	—	Gould	1871	—
52e	—	Peters	1876	—
52f	—	Gould	1871	13 Sr. 2 Zr.
53	II.	Pogson	1853	3 Hn. 17 K. 2,0,10 Sk. 32 Sr.
54	II.?	Burchell	1827	—
54a	—	Thome	1872	—
55	II.	Winnecke	1861	4 Hn. 50,32,26 Sk.
56	II.	Chacornac	1856	—
57	II.	Peters	1865	—
58	II.	Peters	1871	4 Ee.
59	II.	Schönfeld	1856	4 K. 9 P.
60	II.	Boguslawski	1849	3,18,5 Sk.
61	II.	Karlinski	1867	25,14,3 Sk.
61a	II.	Henry	—	—
62	II.	Hencke	1856	12,10,19 Sk. 34 Sr.
63	II.	Harding	1809	2,0,0 Sk. 31 Sr.
63a	IV.	Gould	1871	—
64	II.	Pogson	1853	17 K. 11,14,39 Sk. 32 Sr.
65	II.	Harding	1831	12,0,15 Sk. 5 Sr.
66	II.?	Schönfeld	1866	—
67	II.	Goldschmidt	1857	13 P. 4,0,0 Sk.
68	II.	Maraldi	1704	30,0,4 Sk.
69	II.	Hind	1852	7 K.
69a	II.	Palisa	1880	10 P.
69b	—	Gould	1871	—
70	I.?	Baxendell	1860	—
71	II.	At Bonn	1860	14 Ee. 14 Hn. 6,14,0 Sk.
72	II.	Hencke	1858	10 Ee. 10 P. 51,40,40 Sk.
73	II.	At Bonn	1858	2 G. 0,18,39 Sk. 29 Sr.
73a	—	Schmidt	1867	6 Zr.
73b	II.	Baxendell	1880	16 Ee.
74	V.	Schmidt	1859	5 Zr.
74a	II.	Palisa	1878	—
74b	IV.?	Gould	1871	—
75	V.	Winnecke	1869	11 Hn.
76	II.	Borelly	1872	10 P. 19,12,8 Sk.
77	II.	Harding	1828	12 Ee. 9 Hn. 20 P.

TABLE I. — *Continued.*

No.	H. P.	Name.	R. A. 1875.	Dec. 1875.	Max.	Min.	Per.
			h. m. s.	° ' "	m.	m.	d.
78	2553	S Coronæ	15 16 18	+31 49.1	6.1—7.8	11.9—12.5	361.0
78a	—	Libræ	34 46	—20 46.5	9	<14	—
79	2639	R Coronæ	43 25	+28 32.5	5.8	13.0	Irr.
80	2647	R Serpentis	44 56	+15 30.8	5.6—7.6	<11	357.6
80a	—	V Coronæ	45 4	+39 57.0	7.7	12	360.0
81	—	R Libræ	46 32	—15 51.7	9.2—10.0	<13	723
82	2678	T Coronæ	54 16	+26 16.5	2.0	9.5	—
83	—	R Herculis	16 0 37	+18 42.5	8.0—9.0	<13	319.0
83a	—	W Scorpil	4 28	—19 48.6	10	<13	224.3
84	—	T Scorpil	9 36	—22 39.9	7	<10	—
85	—	R Scorpil	10 12	—22 38.2	9?—10.5	<12.5	223
86	—	S Scorpil	10 13	—22 35.2	9.1—10.5	<12.5	176.9
86a	—	Ophiuchi	14 40	—7 24.0	9.0	<13.5	326
87	—	U Scorpil	15 16	—17 35.3	9?	<12	—
87a	—	Ophiuchi	19 46	—12 8.5	7.5	10.5	365
88	—	U Herculis	20 16	+19 10.8	6.6—7.7	11.4—11.6	408.3
89	2772	g Herculis	24 32	+42 9.6	5	6.2	Irr.
90	—	T Ophiuchi	26 35	—15 51.8	10	<12.5	—
91	—	S Ophiuchi	27 4	—16 53.7	8.3—9.0	<12.5	233.8
91a	—	W Herculis	30 48	+37 35.6	8.0	<14.5	239
91b	—	Urs. Min.	31 40	+72 31.9	8.6	10.5	180?
91c	—	R Draconis	32 22	+67 0.7	7.2	13<	245.9
92	2828	S Herculis	46 13	+15 9.2	5.9—6.8	11.5—12.2	303
93	2833	Ophiuchi	52 30	—12 42.0	5.5	12.5	—
93a	—	V Herculis	53 41	+35 15.5	9.0	11.7	—
94	—	R Ophiuchi	17 0 36	—15 55.5	7.6—8.1	<12	302.4
95	2879	a Herculis	8 57	+14 32.1	3.1	3.9	Irr.
95a	2383	U Ophiuchi	10 12	+ 1 21.0	6.1	6.8	0.9
96	2890	u Herculis	12 42	+33 14.1	4.6	5.4	38.5
97	—	Serpentarii	23 9	—21 22.4	>1	?	—
98	2972	X Sagittarii	39 41	—27 46.8	4	6	7.0
99	3035	W Sagittarii	57 2	—29 35.1	5	6.5	7.6
100	—	T Herculis	18 4 22	+31 0.1	7.2—8.3	11.4—12.1	165.1
101	—	T Serpentis	22 43	+ 6 13.1	9.1—10.0	<12.8	342.3
102	—	V Sagittarii	24 4	—18 20.9	7.5?	9.5?	—
103	—	U Sagittarii	24 32	—19 12.7	7.0	8.3	6.7
104	—	T Aquilæ	39 45	+ 8 36.9	8.8	9.5	Irr.
105	3176	R Scuti	40 49	— 5 50.2	4.7—5.7	6.0—8.5	71.1
105a	—	κ Pavonis	44 3	—67 23.2	4.0	5.5	9.1
106	3193	β Lyræ	45 28	+33 13.0	3.4	4.5	12.9
107	3224	R Lyræ	51 32	+43 47.1	4.3	4.6	46.0
108	—	S Coron. Austr.	52 43	—37 7.2	9.8	11.5?	6.1
109	—	R Coron. Austr.	53 29	—37 7.2	10.5—11.5	<12.5	31
110	—	R Aquilæ	19 0 21	+ 8 2.6	6.4—7.4	10.9—11.2	345.1
111	—	T Sagittarii	9 1	—17 11.2	7.6—8.1	<11	381
112	—	R Sagittarii	9 21	—19 31.5	7.0—7.2	<12	270.0
113	—	S Sagittarii	12 7	—19 15.1	9.7—10.4	<12.7	230
114	3395	R Cygni	33 28	+49 55.1	5.9—8.0	13	425.3
115	—	11 Vulpeculæ	42 26	+27 0.5	3	?	—
116	—	S Vulpeculæ	43 16	+26 58.7	8.4—8.9	9.0—9.5	67.5
117	3434	χ Cygni	45 46	+32 36.0	4.0—6.0	12.8	406.5
118	3436	η Aquilæ	46 6	+ 0 41.2	3.5	4.7	7.2
119	—	S Cygni	20 2 53	+57 37.6	8.8—9.5	<13	322.8
120	—	R Capricorni	4 17	—14 38.2	8.8—9.7	<13	347
121	—	S Aquilæ	5 52	+15 14.9	8.9—9.9	10.7—11.8	147.2

TABLE I. — *Continued.*

No.	Class.	Discoverer.	Date.	Observations, 1885.
78	II.	Hencke	1860	10 Hn. 6 K. 15,50,39 Sk. 35 Sr.
78a	—	Peters	1878	9 P.
79	II.?	Pigott	1795	3 Ee. 5 G. 61,30,26 Sk. 70 Sr.
80	II.	Harding	1826	7 Ee. 1 K. 17 P. 6 Sr.
80a	II.	Dunér	1878	19 D. 3 Ee. 1 En. 27,16,16 Sk.
81	II.	Pogson	1858	—
82	I.	Birmingham	1866	17 B. 13 Hn. 2 K. 3,9,16 Sk.
83	II.	At Bonn	1855	24 Ee. 8 Hn.
83a	II.	J. Palisa	1877	11 P.
84	I.	Auwers	1860	—
85	II.	Chacornac	1853	5 K. 9 P.
86	II.	Chacornac	1854	5 K. 9 P.
86a	II.	Schönfeld	1881	—
87	I.?	Pogson	1863	—
87a	—	Dunér	1881	6 D.
88	II.	Hencke	1860	18,32,22 Sk. 30 Sr.
89	III.	Baxendell	1857	65 Sr.
90	II.	Pogson	1860	—
91	II.	Pogson	1854	1 Hn.
91a	—	Dunér	1880	13 D. 16 Ee. 7 Hn. 10 P.
91b	II.	Pickering	1881	20,17,70 Sk.
91c	II.	Geelmuyden	1876	39 Sr. 9,13,25 Sk.
92	II.	At Bonn	1856	8 Hn. 35,30,39 Sk.
93	I.	Hind	1848	—
93a	II.	Baxendell	1880	12 Ee.
94	II.	Pogson	1853	—
95	III.	W. Herschel	1795	2 Sr. 18 Zr.
95a	V.	Sawyer	1881	4 Sr.
96	III.	Schmidt	1869?	2 G. 12 Sr. 16 Zr.
97	I.	Fabricius	1604	—
98	IV.	Schmidt	1866	26 Sr.
99	IV.	Schmidt	1866	31 Sr.
100	II.	At Bonn	1857	10 Hn. 7,22,14 Sk. 16 Sr.
101	II.	Baxendell	1860	3 Ee.
102	II.	Quirling	1865	—
103	IV.	Schmidt	1866	—
104	II.	Winnecke	1860	—
105	II.	Pigott	1795	3,0,0 Sk. 65 Sr.
105a	IV.	Thome	1872	—
106	IV.	Goodricke	1784	1 Hg. 19 Zr.
107	II.?	Baxendell	1856	67 Sr.
108	IV.?	Schmidt	1866	—
109	II.?	Schmidt	1866	—
110	II.	At Bonn	1856	7 Ee. 13,3,32 Sk.
111	II.	Pogson	1863	35,17,14 Sk.
112	II.	Pogson	1858	6 P. 24,10,10 Sk.
113	II.	Pogson	1860	7 P. —,12 Sk.
114	II.	Pogson	1852	9 Hn. 17 P. 10,8,1 Sk.
115	I.	Anthelm	1670	3 K.
116	II.	Hind	1861	31 Hn. 2 K. 7,0,0 Sk.
117	II.	Kirch	1686	2 En. 22 G. -Hg. 36 P. 29,27,9 Sk. 28 Sr.
118	IV.	Pigott	1784	—
119	II.	At Bonn	1860	9 K. 18 P. 0,2,12 Sk.
120	II.	Hind	1848	—
121	II.	Baxendell	1863	3 Ee. 16 K. 30 P.

TABLE I.—Continued.

No.	H. P.	Name.	R. A. 1875.	Dec. 1875.	Max.	Min.	Per.
			h. m. s.	° ' "	m.	m.	d.
122	—	R Sagittæ	20 8 22	+16 21.0	8.5—8.7	9.8—10.4	70.4
123	—	R Delphini	8 53	+8 42.7	7.6—8.5	12.8	284.0
124	3547	P Cygni	13 11	+37 38.7	3—5	<6	—
125	—	U Cygni	15 44	+47 30.1	7.8?	9.8?	—
126	3557	R Cephei	19 42	+88 45.2	5?	10?	—
126a	—	—Cygni	37 17	+47 41.8	8	12	423.
127	—	S Delphini	37 19	+16 38.4	8.4—8.6	10.4—11.1	275.6
128	—	T Delphini	39 34	+15 56.7	8.2—8.9	<13	331.4
129	—	U Capricorni	41 11	—15 14.4	10.2—10.8	<13	203.5
130	3654	T Cygni	42 12	+33 55.0	5.5?	6?	—
131	—	T Aquarii	43 20	—5 36.5	6.7—7.0	12.4—12.7	203.2
132	—	R Vulpeculæ	58 49	+23 19.5	7.5—8.5	12.5—13.0	137.5
132a	—	Capricorni	21 0 19	—24 25.5	9½	14	—
132b	—	T Cephei	7 52	+67 58.9	5.6	9.5	382
133	—	T Capricorni	15 6	—15 41.4	8.9—9.7	<13	269.4
134	—	S Cephei	36 45	+78 8.6	7.4—8.5	11.5	485
134a	—	Nova Cygni	37 2	+42 18.2			—
135	3845	µ Cephei	39 41	+58 12.4	4?	5?	Irr.
136	—	T Pegasi	22 2 48	+11 55.7	8.8—9.3	<12.5	367.5
137	3981	δ Cephei	24 32	+57 46.6	3.7	4.9	5.4
137a	—	Lacertæ	37 43	+41 43.0	8.6	<13.5	315.
138	—	S Aquarii	50 25	—21 0.6	7.7—9.1	<11.5	279.4
139	4078	β Pegasi	57 45	+27 24.2	2.2	2.7	Irr.
140	—	R Pegasi	23 0 22	+9 52.1	6.9—7.7	12?	382.0
141	—	S Pegasi	14 14	+8 14.2	7.6	<12.2	—
142	4193	R Aquarii	37 21	—15 58.7	5.8—8.5	11?	388.0
143	4234	R Cassiopeiæ	52 4	+50 41.5	4.8—6.8	<12	425.9

## REMARKS.

2. Max. 1885, beginning of February. D.  
6a. Min. 1885, March 14, 9h. 32m. G. M. T.; March 19, 9h. 12m. G. M. T. K.  
12. Max. 1885, February 4. G. Max. 1885, February 11; magn. 2.9. K.  
27a. Max. 1885, February 12. D.  
37. Rising to max. 1885, May 11; magn. 7.3. K.  
38b. Rising to max. 1885, April 17; magn. 10.1. K.  
38c. Max. 1885, January 25±. Min. 1885, January 6.5, February 17. En.  
43. Max. 1885, April 8.8; magn. 9.25 (a double max.?). 1885, December 6±?? K.  
46. Max. 1884, December 30; magn. 10.6. K.  
47. Minima partially observed, 1885, February 20, March 11. Star disappeared in mist near horizon. K.  
53. Max. 1885, June 28; magn. 7.1. Min. 1885, March 10; magn. 13.2. K.  
59. Invisible on each occasion. K.  
64. Max. 1885, May 6; magn. 7.25. K.  
69. Declining. K.

TABLE I. — *Continued.*

No.	Class.	Discoverer.	Date.	Observations, 1885.
122	II.?	Baxendell	1859	25 Ee. 38 Hn. 1 P.
123	II.	Hencke	1859	7 Hn. 18,22,6 Sk.
124	I.	Janson	1600	0,1,16 Sk. 44 Sr. 13 Zr.
125	II.	Knott	1871	8 Ee. 7 En. 12 K. 11 P. 32,43,44 Sk.
126	II.?	Pogson	1856	18 Ee. 7 K. 20,10,12 Sk.
126a	II.	Birmingham	1881	3 En. - Hg. 11 P. 60,50,35 Sk.
127	II.	Baxendell	1860	21 Ee. 4 P. -, -, 21 Sk.
128	II.	Baxendell	1863	14 Ee. 14 K. 19,19,11 Sk.
129	II.	Pogson	1858	9 P.
130	—	Schmidt	1864	48 Sr.
131	II.	Goldschmidt	1861	11 P.
132	II.	At Bonn	1858	7 Ee. 10 K. 2 P. 8,0,0 Sk.
132a	—	Peters	1867	9 P.
132b	II.?	Ceraski	1878	25 Ee. 32 K. 25,30,45 Sk.
133	II.	Hind	1854	5 P.
134	II.	Hencke	1858	31 Ee. 56,60,54 Sk.
134a	I.	Schmidt	1876	—
135	III.?	Hind	1848	1 B. 35 G. 49,25,34 Sk. 22 Zr.
136	II.	Hind	1863	10 P. 0,2,0 Sk.
137	IV.	Goodricke	1784	22 Zr.
137a	—	Deichmüller	1883	4 Ee. - Hg. 11 K. 2 P.
138	II.	Argelander	1853	8 P. 13,1,2 Sk.
139	III.	Schmidt	1847	3 B. 39 Sr.
140	II.	Hind	1848	4 Ee. 4 P.
141	II.	Marth	1864?	0,1,0 Sk.
142	II.	Harding	1811	8 P. 19,8,8 Sk. 18 Sr.
143	II.	Pogson	1853	5 D. 5 Ee. 6 G. 19 P. 41,24,23 Sk.

78. Max. 1885, May 5 $\pm$ ?; magn. 7.6. K.

79. Estimated magn. 5.8 to 6.0. G.

80. 1885, April 20; magn. 11.5. K.

80a. Max. 1885, August. Computed max. 1878, October 21.7, +356<sup>a</sup>.52. E.  
Computed min. 1879, May 3, +356<sup>a</sup>.52 E. D.

85. Past max. 1885, May 11. K.

86. Past max. 1885, May 11. K.

87a. Max. 1885, about end of March. D.

91a. Max. 1885, September. D.

117. Max. 1884, November 23. G.

121. Min. 1885, June 16; magn. 11.0. Star called *T Aquilæ* by Baxendell. K.

125. Max. 1885, May 16; magn. 7.65. K. Max. 1885, middle of July. En.

128. Max. 1885, Aug. 17; magn. 10.3. Star called *S Delphini* by Baxendell. K.

132. Max. 1885, July 20; magn. 8.2. K.

132b. Max. 1885, April 2; magn. 6.3. Min. 1885, September 15; magn. 9.6. K.

135. Near max. 1885, May 11. G.

TABLE II.—ADDITIONAL STARS.

No.	R. A. 1875.	Dec. 1875.	Observations, 1885.	Rem.
	h. m.	° ' "		
1	0 6.8	+14 30	3 B.	A.
3	15.4	-20 45	3 M.	
—	35.9	+40 37	13 D. 27 Ee. - Hg. 17 Hn. 47 P.	
9	37.8	+ 6 37	6 P.	
21	1 6.2	+80 53	3 M.	
23	7.7	+34 57	3 M.	B.
25	15.0	+ 9 2	5 P.	
31	19.5	- 4 37	3 M.	
37	25.7	- 7 22	3 M.	
—	28.2	+11 55	5 G.	
43	33.5	-29 40	3 M.	C.
45	39.1	+ 7 56	3 M.	
47	47.7	+ 8 10	4 B. 3 M.	
57	2 0.8	- 9 11	3 M.	
59	10.4	+58 22	3 M.	
61	15.2	+54 47	3 M.	D.
63	19.0	+ 9 56	3 M.	
—	28.2	-13 38	8 Sr.	
—	49.3	+58 14	42,35,45 Sk.	
73	3 37.6	+ 9 0	4 P.	
77	41.8	- 0 17	1 M.	E.
81	46.5	+ 7 24	3 G. 5 M.	
85	49.5	+39 39	3 M.	
87	57.8	+23 38	5 P.	
91	4 10.5	-10 24	3 M.	
93	14.6	+19 31	3 K. 5,5,3 Sk.	F.
117	5 1.4	- 8 49	1 M.	
123	5.3	+ 0 22	1 M.	
129	6.6	- 0 15	1 M.	
145	28.3	+10 10	15 G.	
151	29.3	- 3 20	1 M.	G.
—	48.4	+20 9	3 D. 7 G. 6 P. 5 Sr.	
—	7 16.2	+23 47	26,-0 Sk.	
205	8 2.4	+19 48	5 P.	
—	49.1	+12 7	- K.	
—	51.5	+11 18	- K.	J.
229	9 20.1	+14 50	3 M.	
243	30.4	+15 48	2 M.	
293	10 45.5	-20 35	4 M.	
303	11 10.0	- 3 22	5 M.	
311	12 7.5	+ 0 17	3 M.	K.
315	10.7	+80 49	2 M.	
327	24.0	+ 5 6	3 M.	
331	26.9	-19 56	1 M.	
337	32.7	+17 12	3 M.	
339	32.9	+17 11	1 M.	L.
348	44.6	+82 23	4 M.	
353	13 3.2	- 9 40	3 M.	
361	24.0	- 8 55	3 M.	
375	47.8	+11 41	4 M.	
381	56.4	- 1 47	7 M.	K.
—	14 15.4	- 1 25	9 B.	
—	24.7	+39 36	25 D.	
413	45.4	-11 49	6 M.	L.

TABLE II. — *Continued.*

No.	R. A. 1875.	Dec. 1875.	Observations, 1885.	Rem.
	h. m.	o ' "		
429	15 10.7	— 3 43	5 M.	
447	36.5	—10 31	3 M.	
459	16 1.2	—21 11	10 P.	
465	9.1	+11 50	3 M.	
471	22.4	—19 14	3 P.	
479	31.7	+72 32	4 M.	
483	44.7	— 5 58	5 M.	
491	53.2	— 4 2	3 M.	
503	17 37.6	—18 36	3 M.	
509	18 2.7	+28 44	18 B. 87 Hn. 15 Zr.	
—	20.5	+38 40	2,4,3 Sk.	M.
517	28.0	+36 54	5 M. 3,5,5 Sk.	N.
—	38.5	+36 50	3,4,8 Sk.	O.
—	39.1	+39 11	3,6,7 Sk.	P.
521	43.1	— 8 3	3 M. 6,5,12 Sk.	Q.
529	52.8	+14 12	2 M.	
535	57.7	— 5 52	— K. 2 M. 5,5,11 Sk.	R.
537	59.8	+56 63	3 M.	
543	19 19.0	—21 30	3 M.	
545	23.9	+ 2 39	3 M.	
549	27.1	+17 28	6 Ee. 3 M.	
555	35.3	+12 53	10 Ee. 3 G. 1 M.	S.
557	37.9	+35 55	3 M.	
561	39.1	+33 51	3 M.	
—	39.9	+34 7	2 M.	
—	50.3	+16 17	25 G. 16 Sr.	T.
567	20 7.1	—22 21	7 P.	
—	9.8	—21 42	20,12,20 Sk.	U.
573	19.7	+ 9 39	3 M.	
575	23.6	—12 39	3 G. 3 M.	
—	24.3	+39 34	18 En. — K.	V.
585	39.6	— 0 48	3 M.	
—	39.7	+17 38	14 G.	W.
589	42.6	+45 36	5 M. 37,24,14 Sk.	X.
591	44.5	+45 23	3 M. 37,24,14 Sk.	Y.
—	46.1	+27 47	7 G. 37 Sr.	Z.
595	59.6	+66 13	3 M.	
597	21 0.1	+67 41	3 M.	
601	1.4	—21 51	7 P.	
603	7.9	+67 59	2 M.	
607	12.2	+66 6	3 M.	
—	31.3	+44 49	54 G. 55 Sr.	AA.
—	38.2	+37 27	0,0,14 Sk.	
613	45.2	+ 6 4	3 M.	
615	56.5	—17 14	9 P.	
—	22 29.3	— 8 15	— K.	BB.
—	31.6	+57 47	8 En.	CC.
635	23 14.8	+55 26	3 M.	
645	33.3	— 1 26	6 M.	
—	39.9	+ 2 47	1 G.	DD.
653	54.9	+59 40	1 M.	

## REMARKS.

- A. New star in the nebula of Andromeda, announced by Hartwig.
- B. This star is 100 *Piscium*. Variation discovered by Borelly. Near a maximum, 1885, November 30. G.
- C. Discovered by Sawyer in 1884. Period not determined.
- D. DM.  $+58^{\circ}$  539.
- E. Discovered by Gore in 1885.
- F. The observations show a variation of about half a magnitude. The star has been called T *Orionis*. G.
- G. Discovered by Gore in 1885. Magn. 6.15, December 13, 1885. G.
- H. DM.  $+23^{\circ}$  1699. Sk.
- I. 60 *Cancr.* K.
- J. DM.  $+11^{\circ}$  1954. Variation suspected by Baxendell. K.
- K. 103 *Virginis*. B.
- L. This star has been called V *Bootis*. Max. 1885, June 1; magn. 7.2. Min. 1885, January 28, October 23; magn. 9.4. Computed max. 1884, September 3,  $+266.5$  E. Computed min. 1885, January 29,  $+266.5$  E. D.
- M. Birmingham 442. Sk.
- N. Birmingham 448. Sk.
- O. Birmingham 458. Sk.
- P. Birmingham 459. Sk.
- Q. Birmingham 464. Sk.
- R. Birmingham 483. Sk.
- S. About magn. 8, 1885, August 19, September 9, November 4. G.
- T. Discovered by Gore, 1885. Confirmed by Espin and Sawyer. Variation from about magn. 5.6 to 6.4. Period short, about  $8\frac{1}{2}$  days (G.), 8 days (Sr.).
- U. Birmingham 545. Sk.
- V. DM.  $+39^{\circ}$  4208. Found 1885, July 9, as a splendid red star, magn. 7.9, since varying to 9.2; no period found; diminishing irregularly. En. Below magn. 8, 1885, August 13, September 7, September 9.
- W. Birmingham 569. Discovered by Espin and confirmed by Gore. Period perhaps  $111\pm$  days. G.
- X. DM.  $+45^{\circ}$  3271. Sk.
- Y. DM.  $+45^{\circ}$  3289. Sk.
- Z. Discovered by Sawyer, 1885, and confirmed by Gore. Period 4.437 days. Sr.
- AA. Birmingham 587. Discovered by Gore, 1885, and confirmed by Sawyer. Near max. 1885, January 1, August 19; near min. 1885, June 9. G. Period  $120\pm$  days. Sr.
- BB. Variation suspected by Hind. K.
- CC. DM.  $+57^{\circ}$  2568. Fine orange red. Observed variation from magn. 7.0 to 8.0. Period probably short. En.
- DD. 19 *Piscium*. Magn. 5.5, October 3, 1885. G.

Professor Safarik also reports the following numbers of observations of suspected variable stars, which are given in the same form as in the tabular statements: star in *Auriga*, 0,0,1; in *Canis Major*, 0,0,2; in

*Capricornus*, 0,0,13; in *Monoceros*, 0,3,3; two in *Ophiuchus*, 0,14,9; in *Perseus*, 0,0,8; in *Virgo*, 0,0,9.

He has made observations of the minor planets as follows: Ceres (1), 6,19,23; Pallas (2), 0,0,24; Juno (3), 4,23,12; Vesta (4), 0,0,4; and observed the periodical comet Pons three times in December, 1883, and eight times in January, 1884.

The observations of asteroids just mentioned deserve attention, and it is to be hoped that other observers will adopt the practice of observing such objects, and of including them in their statements with regard to variable stars. The instance of Iapetus shows that the variations of a body shining by reflected light may become an interesting object of study, and may instruct us with regard to its period of rotation. Again, supposing it to be proved, either that a certain asteroid varies only in accordance with its distance from the Sun and from the observer, or that its other variations have a sufficiently definite character to allow them to be computed, it would form a valuable instrument of comparison between widely separated stars. It is probable that stellar magnitudes, as estimated, or even as measured by many kinds of photometric apparatus, are subject to systematic errors dependent upon the relative frequency of stars in different parts of the sky. These errors might be detected and eliminated by the comparison of asteroids with the stars differing but little from them in brightness, among which they were apparently moving at different times.

## XXI.

## ON THE METHODS OF STUDY OF THUNDER-STORMS.

BY W. M. DAVIS.

Communicated February 10, 1886.

DURING the past summer the New England Meteorological Society undertook a special series of observations on thunder-storms, and while preparing the blanks and studying the records there has been occasion to examine similar investigations elsewhere, from which it appears that there is some diversity as to matter of observation and method of discussion. In order to make the contrast among the several systems better understood, I may first state briefly the peculiar features of thunder-storms, and then explain why a special service of numerous volunteer observers is needed to detect their structure and mechanism.

*General Phenomena of Thunder-storms.*—In the first place, many of the thunder-storms that pass over us are so small that they easily slip between the Signal Service stations, without even being heard there. Such a one was the violent thunder-squall of July 21, 1885, that came early from New York, and traversed New England at the rate of nearly fifty miles an hour; it crossed the Hudson about eight o'clock in the morning, quite unobserved from New York City or Albany; it ran along eastward on the northern boundary of Connecticut, passing north of New Haven and New London, and south of Boston, probably in sight from these stations, but too near their horizon to attract attention; finally, it crossed from Plymouth to Provincetown, Massachusetts, and went out to sea about half-past one o'clock, and was heard of no more. It would have been practically unknown, had not our observers determined its path by means of their fifty odd reports.

Larger thunder-storms stretch in long, narrow belts over a considerable distance, advancing sideways or obliquely across the country. These often enough pass over the Signal Service stations, but, even if fully observed there, many of their most characteristic features would remain undetermined. Besides, the observers at the signal offices have much routine work to do, and cannot well be called upon to perform extra and irregular duties. The considerable amount of non-

instrumental observation that a fully developed thunder-storm needs, may be inferred from the following description of the phenomena accompanying such a storm, while passing through the storm-belt at right angles to its length. The earliest forerunner of the storm is the high cirro-stratus overflow, reaching far ahead of the rain: as this rises above the western horizon, the outlines of massive gray "thunder-heads," or cumuli, appear beneath it; they reach to a great height, and are seen towering aloft as they approach. Towards the base they are very dark; but often at the lower front margin of these heavy clouds there appears a ragged fringe of gray squall-cloud, much agitated, and below this is the falling rain. All these clouds should be examined to detect their motion and growth. As the storm comes nearer, and the thunder grows louder, the wind squall may sometimes be recognized in the distance by the dust that it raises; it strikes suddenly, often with destructive force, and quickly passes on as the rain begins. This squall is not an invariable accompaniment of thunderstorms, and it is yet to be determined why it is sometimes present, sometimes absent. The temperature falls rapidly as the rain comes; for the temperature of the rain, and especially of the hail that often accompanies it, is much lower than that of the air. Much is hidden now by the falling rain, but, as it passes, the lower clouds appear and rapidly break away, showing brighter clouds or clear sky and sunshine in the west. The high cirro-stratus is then seen on the rear of the storm: it often shows the curious festoon-clouds on its lower surface. As the sky clears, the temperature returns towards its normal value.

The altitude, dimensions, and motion of all these many parts manifestly offer plenty of material for systematic study; and all weather services agree that many observers are needed in such work. The average distance between the stations must be a small fraction of the dimensions of the storm, or else features of importance may escape notice.

*Plan of Observations.*—In laying out the task for the volunteer assistants, no predetermined hours for occasional synchronous observations can be found that serve well in this work; times set before hand would too often fail to catch the swiftly passing storms. Records must be made chiefly at times announced by the storms themselves. It would take the greater part of an observer's attention for the two or three hours of a storm's passage to detect and record all its noteworthy peculiarities, and this is much more time than most volunteer observers can give. But the interest, time, opportunity, and ability of observers are so varied, that what is easily accomplished by one is far out of reach of another. We have therefore given detailed instructions to the

better, more devoted observers, so as to lead them on to their own improvement as well as to ours ; while we have offered only the very simplest form of record to those who are willing to do something, but who are unable to do much, or who would be discouraged at the sight of a page or more of printed explanations. So far as I know, no other services thus classify their observers : this cannot be because they have enough of the highest class to serve all their needs, for their observations are generally very elementary as to material, and in many cases are insufficient in number. Doubtless it would be best to have all observers of one uniform and high standard ; but this is quite out of the question in a volunteer service. Our observers were therefore divided into three classes last summer, and, in attempting the work again this year, it seems best to separate the classes still further ; not by having more than three classes, but by reducing the demands on Class A, and by asking for more from those whom last summer's work has shown to be painstaking and close observers.

Before comparing the observations on special phenomena desired by different services, another point may be mentioned which is, I believe, peculiar to the instructions of our New England Society. This is the attempt to obtain material for synchronous maps of storms, without announcing beforehand the hours for observation ; and although it did not fully succeed, from lack of observers, it may be regarded as a distinct improvement, and one well worth retaining in a second year's work. Observers of Classes B and C were asked to take record of temperature, wind, &c., every *even* half or quarter hour *during the storm*. This is a heavy task, but in return it gives us data for the construction of numerous synchronous maps at short intervals, showing not simply the inferred advance of the storm-belt, but the actual attitude of all the accompanying phenomena for the several times of record. The advantage of taking hours thus marked out by the storm over any hours appointed before hand is apparent at once ; and the importance of the method may be estimated by considering the great advance that was accomplished when it was introduced in the study of cyclonic storms.

In deciding what elements of the storm shall be observed most fully, it must be first agreed by what feature the advance of the storm shall be defined. In Italy, Ferrari places the storm by the attitude of its "maximum phase" where the thunder is loudest. In Bavaria, Von Bezold takes the time of the first thunder for his guide, and draws "isobrontal" lines through points where it is heard at the same time. The first rain has thus far been used in our reductions, and with very

satisfactory results. Evidently the storm front, however determined, must be defined by a feature easily recognized by all observers; for the usefulness of the relatively few detailed records of the higher class observers depends largely on the accuracy with which they can be placed in their proper position with respect to the storm front, as determined at numerous stations by the simple records of the lower class. It is therefore an important matter to choose what shall be adopted as the guide-observation, as this defines the simplest task that can be set.

The time of first audible thunder is not satisfactory. It comes without warning; it is faint; it is not equally perceptible to observers in different situations; even if well observed, it measures a variable distance from the storm-belt, for the flashes that cause the thunder must be of unequal intensity; finally, it is too distant a product of the storm, and should be replaced by something more immediately connected with the line of action. As a guide, it therefore does not seem serviceable. In storms where no rain reaches the ground, the first and loudest thunder-claps are of value; but such storms are exceptional, and of small importance.

The last thunder is a troublesome thing to note, and it will probably be omitted in the coming summer. The loudest thunder is very useful as a mark of the middle belt, but it is not always accurately definable; still, it is almost or quite as good a guide as the first rain. But thunder has its chief value in calling the observers to their work; as soon as it is heard, record it, and then watch for what follows.

The rain front in well-developed storms is on the whole, I believe, the best guide to their advance across country. The observer is generally on the watch for its arrival, as the thunder in nearly all cases precedes it. It can often be seen coming just before its arrival, and, thus prepared, the observer may note its time within half a minute without difficulty. Even if no thunder is heard before it, the darkening approach of the rain clouds is generally sufficient to call one's attention from other occupation. The following records show the measure of agreement that may be expected. They are taken from stations in northeastern Rhode Island, where observers were close together.

In the first example, a loud thunder-clap evidently called the attention of all the observers, and in that case gave more closely accordant records than the time of first rain. In the second example, the stations are arranged almost in geographic order, and show an excellent sequence of rain times. The agreement is indeed exceptionally good.

## July 9.

	First Thunder.	Rain.	Loudest Thunder.
Pawtucket,	5.52	6.03	6.47
Providence, a,	5.41	6.05	7.03
b,	6.15	6.10	7.00
c,	6.20	6.12	7.00
d,	6.—	6.08	7.02

## July 21.

Woonsocket,	12.00	12.20	12.24
Ashton,	11.50	12.25	12.20-12.40
Pawtucket, a,	12.15	12.27	12.31
b,	12.17	12.29½	12.35
Providence, a,	12.19	12.27	12.35
b,	12.05	12.28	12.34
c,	12.08	12.28	12.25
d,	12.15	12.30	12.38
e,	12.—	12.30	12.35
Silver Spring,	12.11	12.35	—

*Methods of Observation elsewhere.*—We may now consider the demands made upon observers by various services where the systematic study of thunder-storms has been undertaken: at the same time, a few notes are added on the general standing of the work in several countries.\*

FRANCE. System founded by Leverrier in 1865; reductions in charge of Fron, and now published in the *Annales du Bureau central météorologique*. As an incentive to observation, a large number of maps illustrating the paths of certain storms were distributed to the observers during the first season's work. I do not know how far this practice has been continued. There have been over one thousand observers in recent years.

Observations: time of first, loudest, and last thunder; direction of storm's appearance and disappearance; velocity and direction of clouds; force and direction of wind; intensity of lightning, thunder, rain, hail; direction of distant lightning; general notes on the appearance of the storm, and on its injurious effects.

Intensity is expressed on a scale of six; direction is observed to octants. The records are made on a quarto page, and are sent free, folded but not sealed, through the mail, to the departmental prefects, by whom they are discussed before finally going to Paris.

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\* I am indebted to Mr. A. Lawrence Rotch for opportunity of examining his collection of "forms" for observation, from which many of these notes are taken.

**NORWAY.** Observations were begun in 1867 under the direction of Professor Mohn. The results are published in the *Videnskabs Forhandlinger*, at Christiania, beginning in 1868. An abstract of them in French (from which these notes are taken) is given in certain volumes of the *Atlas météorologique de l'Observatoire de Paris*. In 1868 there were 270 observers.

Observations: time of beginning and end of the storm; its first and last direction; the direction and velocity of wind and clouds; the intensity of lightning, thunder, rain, and hail; remarks on the damage caused by the storm.

**RUSSIA.** The study of thunder-storms in this country was initiated in 1871, by the Imperial Society of Geography. The observations are reduced by Klossovski, Professor in the University at Odessa, who has published a memoir thereon in Russian, and an abstract of it in French, *Les Orages en Russie*, Odessa, 1886. I have seen only the latter: it does not contain statistics as to the number of co-operating observers.

Observations: no instruments required; time of beginning and end of the storm; direction of first and last appearance; intensity of lightning and thunder; intensity and duration of rain and hail; direction and velocity of wind and clouds.

**BELGIUM.** Observations were begun on a small scale in 1867, and extended in 1877 to over eighty observers. The reductions have been made by A. Lancaster, and published in the *Annales de l'Observatoire Royale de Bruxelles*; also in abstract in the *Annuaire*, issued by the same observatory.

Observations: the plan of work is very similar to that followed in France.

**ITALY.** Schiaparelli began the systematic study of thunder-storms in Northern Italy in 1877, the results appearing in the publications of the Royal Observatory of Brera, in Milan. In 1880, the work was taken in charge by the Central Meteorological Office in Rome, and extended over all parts of Italy; the observations for 1880 and 1881 are discussed in great detail by Dr. Ciro Ferrari, and form heavy quarto volumes in the *Annali della Meteorologia*, with numerous maps and diagrams.

Observations (in later years): beginning and end of the storm, and its "maximum phase"; direction of its motion; direction and force of winds; intensity of thunder, lightning, rain, and hail; extent of sky covered by storm; if the observer have instruments, records are desired of rain-fall, temperature, humidity, and pressure.

Records are made on franked postal cards, that are sent first to the meteorological station in the chief town of the province, and afterwards forwarded to Rome.

BAVARIA. Observations begun by Von Bezold in 1879; aided after 1880 by Von Schoder in Würtemberg. The results are published, with other records of the Bavarian service, in the *Beobachtungen der meteorologischen Stationen in Baiern*. In 1879, 279 observers took part in the work, and 252 in 1882; after the first year about 60 observers were added in Würtemberg.

Observations: time and direction of heat-lightning; time of first and last thunder, rain, and hail; direction of storm's advance; direction and strength of the wind before, during, and after the storm; notes on damage caused by the storm. Reports are made on franked postal cards.

NETHERLANDS. Work directed by the Royal Meteorological Institute at Utrecht; observations in charge of, and reduced by Snellen; about three hundred observers in 1884.

Observations: distance of the storm; time of the first, loudest, and last thunder; direction and velocity of clouds; direction and force of the wind before, during, and after the storm; time of first and last rain and hail, and their strength; damage by storm.

Intensities on scale of five. The record is made on a quarto page, that goes free through the mail.

SAXONY. Study of thunder-storms instituted by Bruhns in 1880; now directed by Schreiber at Chemnitz.

Observations: time and direction of first appearance of storm, and of first and last lightning, thunder, and distant rain; time of first and last local rain and hail; time and direction of clouds (kind not specified) passing zenith, or direction of their motion if they do not reach zenith; wind before, during, and after the storm. A special card is provided for record of hail-storms.

CENTRAL GERMANY. Observations made by the *Verein für landwirthschaftliche Wetterkunde*, under the direction of Assmann, beginning in 1880. The results appear in a pamphlet, *Die Gewitter in Mitteldeutschland*, by Assmann. There were over two hundred stations the first year, and about six hundred in 1885.

Observations: direction and intensity of storm; time of first and last thunder, and its intensity; many notes on appearance, direction (up, down, or horizontal), and form of lightning flashes, and on lightning strokes; time of first and last rain and hail, with their amount; direction and strength of wind before, during, and after the storm; notes on dust-squall preceding the storm.

Intensity on a scale of three (0, 1, 2); wind force on scale of twelve. No temperature records. Especial attention is given to the appearance and effects of lightning. Reports are made on postal cards.

SWITZERLAND. Observations systematically begun in 1883; reduced by Mantel and published in the *Annalen der schweizerischen meteorologischen Central-Anstalt*. About 140 stations besides the regular stations of the Swiss weather service. 2,689 reports in 1883.

Observations: time of first and last thunder; of passage over zenith; of beginning and ending of rain and hail; direction of storm's origin and disappearance; direction and force of wind before, during, and after the storm; notes on rain-fall and damage by storm.

Intensity on a scale of six; direction recorded to octants; no observations of temperature. The records are made on franked postal cards.

UNITED STATES SIGNAL SERVICE. Investigation of thunderstorms by volunteer observers, organized by Prof. H. A. Hazen in 1884; records of more than 13,400 storms were obtained for this year, and a report thereon is to be sent to all observers.

Observations: thunder, first, loudest, and last; direction of storm, coming from and going to; time of first and last rain and hail, and amount; direction and force of wind before and after storm; distant lightning; and remarks.

"Thunder-storms twelve hours apart may be taken as separate storms." Intensities on scale of five. Reports are made on a special "penalty card," addressed to the Chief Signal Officer of the Army.

In reviewing the requirements thus summarized, the absence of a sufficient correlation of the several objects of observation, and the general omission of temperature records, seem to me serious defects in the plan of work. Certainly the relation of temperature to wind, of surface wind to cloud-motion, of wind and clouds to rain, etc., can be much better determined if at certain times records are taken of *all* of these different phenomena. We have therefore aimed to secure observations of wind, temperature, rain, clouds, etc., all together, several times during every storm; the times being determined by the occurrence of the first thunder, the first wind-squall, the first rain, the loudest thunder, and the last rain; and also by the even half or quarter hours, as already described. Our records as proposed for the coming summer may therefore be thus summarized.

*Summary of Instructions to New England Observers. — Class A. — Required:* time and direction of first and loudest thunder, whether rain falls or not; time of first, heaviest, and last rain, and estimated amount, whether with thunder or not; intensity of storm on scale of

five. *Requested*: time and amount of hail; time and direction of heat-lightning; notes on wind.

*Class B.* — *Required*: time and direction of first and loudest thunder; temperature, wind (force and direction), and sky at time of first thunder, and then every even half or quarter hour (e. g. 3.00, 3.30, 4.00, etc.) as long as thunder is heard; time, direction, and force of wind-squall, and its temperature; time of first, heaviest, and last rain, its estimated amount, and temperature of air at its beginning and end. *Requested*: notes on violence of rain at various times; frequent observations (even every minute) of temperature during squall; heat-lightning, lightning strokes, and notes on clouds.

*Class C.* — In addition to the requisitions in Class B, observations are here desired on clouds; first appearance and motions of cirro-stratus, cumulus, squall-cloud, festoon-cloud; appearance of distant storms; determination of growth or dissolution of clouds by watching changes at their margins; angular altitude and direction of same clouds from time to time as storm approaches, giving basis for determination of altitude when velocity is known; sketches of clouds; self-registering instrument of some kind, and observations of humidity; photographs of clouds and lightning.

It is not intended that Classes B and C should be rigidly divided; slight changes can be made at the observer's pleasure, but every one must do at least the requirements of Class A. Change of station is also permitted, as we thus gain more than we lose; but permanent residence through the summer is desirable.

It is often nearly as important to know that a storm did not appear at a certain station, as to have a record of it. It is therefore proposed to ask all observers to keep a very simple journal, stating for every day merely whether it was clear, fair, cloudy, rainy, or stormy, and sending in this record at the end of every month. This will insure continuous record, and will at the same time give data for the sharp limitation of storm areas; actual denial of storm being much safer for this purpose than simple absence of report.

I am well aware that the tasks here set are rather severe, but the experience of last summer justifies the expectation that they will be well borne. There is no question whatever that every post-office town in New England contains residents fitted and ready to undertake the records of Class A; the difficulty that we encounter is not in persuading them to do the work, but in finding the right persons. An essential in the scheme is therefore a much greater notoriety than is needed in most scientific investigations; for this we count largely

on newspaper notices, on circulars to members of our society, and to co-operating observers, and in some cases on circulars to postmasters; but in this day of many circulars, they give an uncertain dependence. Members in Classes B and C are enlisted directly or by promotion from A, and include many careful observers, whose interest in the society is a great gain in its work. Indeed, our relation to a body of intelligent correspondents, thus enrolled in all parts of New England, is a most valuable assistance in a variety of ways. We can at any time address them on special questions, and feel fairly sure of interested attention to our requests: for example, in a recent attempt to trace out the limits of an earthquake in southern New Hampshire, I have had much assistance from our volunteer observers of thunder-storms. At the same time, we may feel that the attention thus awakened to matters of a scientific nature constitutes one of the results that we desire to reach; for in the constitution of our society its object is announced to be "the cultivation of meteorological science in New England."

*Discussion of Observations.*—Until the systematic observations were begun in France, most investigations of thunder-storms were devoted to studying their electrical action, to the neglect of their mechanism. This was much as if a physicist should carefully examine the peculiarities of electric sparks, but neglect to study the construction of the machine that produced them. There were, of course, exceptions to this practice, but they were distinctly exceptions. Since the establishment of systematic observations, it has generally been customary to present their results in the form of averages of occurrence according to months, hours, and places; also in averages of direction and velocity of motion, and attitude with respect to the neighboring and controlling centre of low pressure; and again in maps that represent the path of the storm across the country. But while these statements are of much value and interest, they generally consider the storm only as a whole. More detailed study is required to determine the relation of the different parts of the storm, the mechanism of its winds, the distribution of its temperature, pressures, clouds, and electrical phenomena. Some may, however, say, on first approaching this question, Do thunder-storms possess sufficiently persistent features to admit of a regular classification of their parts? The results of European observations—and especially of those discussed by Dr. Ferrari of Rome—answer this question very definitely in the affirmative. We know that cyclonic storms have been found susceptible of detailed dissection, and that their several parts appear with much regularity in

successive storms. Much valuable work has been done of late years in thus showing the average distribution of the meteorological elements in areas of low pressure. A similar work needs yet to be carried to completion for thunder-storms.

Three observations a day are sufficient to define the slow weather changes of the large cyclonic storms; but in thunder-storms observations should be taken every fifteen minutes at most, that is, at the rate of ninety-six times a day, so rapid is the motion of these storms in comparison to their size. A simple method of portraying a storm, thus observed at numerous stations, would be the construction of synchronous maps of all its elements: thus the storm as a whole is seen passing over the country. But even then it is not easy to bring all the details of many maps into a single mental picture; and, moreover, the unfortunate lack of observations must for some time yet make these separate maps very imperfect. Some method of *composite portraiture* is needed that shall throw all the observations into their proper position with respect to some controlling line, such as the storm-front, and at the same time allow the records of one station to supply the deficiencies of another. I have attempted to accomplish this in the following way. The attitude of the storm-front (rain-front) is first determined by charting all the times of rain beginning, and drawing lines to show the position of the front for every even quarter of an hour; the direction and velocity of advance are also thereby determined, and generally, in the best developed storms, a certain line may be chosen to represent the middle path of the storm: the average line of rain-front and the middle path are taken as axes of co-ordinates; time intervals before and after the rain beginning serve as abscissas, while distances north and south of the middle path are ordinates; and the ratio of abscissas to ordinates is known as soon as the average velocity of storm progress is determined. The axes thus chosen are next drawn on a sheet of tracing-paper: now if this sheet be laid upon a map of the region traversed by the storm, and moved along in the direction of the storm's advance (the line of middle path being coincident on the two), it (the tracing-paper) may be taken as representing the storm stratum on its way across the country: every station that furnishes a record may be imagined to trace a line on the storm stratum about parallel to the middle path, and intersecting the rain-front to one side or the other of the middle path, at a distance from it measured by a positive or negative ordinate; and all observations can be placed somewhere on the lines thus traced, their distance in front or behind the rain-front being measured by positive or negative

abscissas. In practice, a simple method of proceeding is adopted: lines are drawn on the storm stratum (tracing-paper) to represent the path of every station through the storm, and the name of the station is written at one end of its line: then a time scale is prepared to measure the abscissas, its unit being the average distance traversed by the storm in an hour; for a storm moving from west to east, as is the general rule, the scale is numbered from right to left; it is next laid on a certain station line, parallel to the middle path, and placed so that the time of rain beginning for this station falls on the rain-front line; then all the observations from that station can be marked down opposite their proper hour and minute on the time scale, and they will thus fall in their proper place in the storm. After plotting a good number of reports in this way, the composite portrait shows that the area an hour or so in front of the rain is occupied with records showing high temperatures, clear sky with clouds from which thunder is heard rising in the west; gentle winds, as a rule from a southerly quarter; nearer the storm the clouds cover more of the sky, and the temperature falls a little; close in front of the rain the wind-squall appears, blowing out from the storm; as the rain is reached, the wind dies away, the temperature falls rapidly, the thunder grows louder, and lightning strokes appear; half an hour or more, with rain still falling gently, the western clouds break up, and blue sky appears; the temperature rises slowly, and the thunder dies away as the storm moves off; and rainbows appear on its back as the sun shines out. It soon becomes evident that there is really a systematic distribution of certain elements of the storm that are susceptible of legitimate averaging; and from their graphic representation in the composite portrait, the proper areas and intervals for averaging may be chosen. In this way, the fullest use may be made of the most varied records.

## XXII.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL  
LABORATORY.

## THE DYNAMIC ACTION OF AN ELECTRIC CURRENT.

BY HAMMOND VINTON HAYES.

Communicated November 11, 1885.

IN the measurement of the strength of an electric current by a galvanometer, the formula usually employed is

$$C = \frac{Hr}{2\pi n} \tan \theta.$$

This formula is strictly true only when the needle is upon the axis of the coil, which must consist of a small number of turns of wire. If the needle is not upon the axis of the coil, this formula no longer holds good, and a new one must be determined by the use of elliptic integrals or by zonal harmonics. The method by zonal harmonics is the simpler of the two, but is rendered very difficult by Maxwell in his Treatise on Electricity and Magnetism. Maxwell also devised a method of approximation to find the potential at any point, when a coil of large cross-section was employed. His treatment of this is almost incomprehensible. It is hoped that in the following paper the errors in Maxwell's formulæ have been eliminated, and that the subject has been brought within the grasp of all.

Let us first take a current of electricity passing through a single

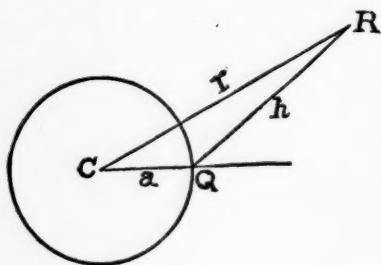


Fig. 1.

turn of wire in the form of a circle, and find the potential due to this current at any point. Since, by Ampère's theorem, the magnetic action of a closed current is equal to that of a magnetic shell of the same contour, we will for simplicity replace the circuit by that part of a spherical shell which has the circuit

for a boundary. Let, now, the surface density of such a spherical magnetic shell be  $\phi$ , its radius be  $a$ , and let there be a unit magnetic pole  $R$  at distance  $r$  from  $C$ , the centre of the sphere. Moreover, let  $dS$  be any small element at  $Q$ , and at a distance  $h$  from  $R$ . Let  $p = \frac{1}{h}$ . Let  $O$  be the value of the flow, or the surface integral, at the point  $Q$ . Then the mutual potential of the magnetic shell and a unit pole placed at  $R$  will be

$$\Omega = \int \frac{dO}{da}.$$

But, since  $h$  is the distance between the element and the point  $R$ ,

$$O = \int \frac{\phi}{h} dS = \int p \phi dS;$$

whence by substitution we find

$$\Omega = \iint \phi \frac{dp}{da} dS.$$

But  $p$  is a homogeneous function of the degree  $-1$  of the radius  $a$  and of the distance  $r$  from  $R$ , which gives the conditions,

$$a \frac{dp}{da} + r \frac{dp}{dr} = -p;$$

or,

$$\frac{dp}{da} = -\frac{1}{a} \left( p + r \frac{dp}{dr} \right) = -\frac{1}{a} \left( \frac{d(pr)}{dr} \right);$$

substituting, we have

$$\Omega = - \iint \phi \frac{d(pr)}{dr} dS.$$

But if  $V$  is the potential at  $R$  due to the small element of the shell  $dS$ , we shall have

$$V = \iint \phi p dS;$$

therefore

$$\Omega = - \frac{1}{a} \frac{d(rV)}{dr}, \quad (a.)$$

which is the expression for the potential due to a magnetic shell of unit strength.

We must now find  $V$ . Let  $AB$  be the coil bounding the magnetic shell, and let  $CZ$  be the axis of the coil, and consequently normal to the shell. Let us take a point  $Z$  upon the axis, distant  $z$  from the centre  $C$ . The potential at  $Z$  due to any small element  $dS$  at  $P$  upon the surface of the magnetic shell is

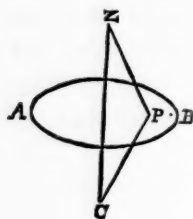


Fig. 2.

$$\frac{dS}{ZP};$$

but

$$ZP = (z^2 + a^2 - 2az \cos \alpha)^{\frac{1}{2}};$$

calling  $\cos \alpha = \mu$ ,

$$\frac{1}{ZP} = (z^2 + a^2 - 2az\mu)^{-\frac{1}{2}},$$

$$\frac{1}{ZP} = \frac{1}{z} \left( 1 + \frac{a^2}{z^2} - 2\frac{a}{z}\mu \right)^{-\frac{1}{2}};$$

also,

$$\frac{1}{ZP} = \frac{1}{a} \left( 1 + \frac{z^2}{a^2} - 2\frac{z}{a}\mu \right)^{-\frac{1}{2}};$$

calling  $\frac{a}{z} = h$  and  $\frac{z}{a} = h_1$ , we have

$$\frac{1}{ZP} = \frac{1}{z} (1 - 2h\mu + h^2)^{-\frac{1}{2}}, \quad [\text{Equa. I.}]$$

$$\frac{1}{ZP} = \frac{1}{a} (1 - 2h_1\mu + h_1^2)^{-\frac{1}{2}}. \quad [\text{Equa. II.}]$$

Developing equation [I.] by the binomial theorem, we have

$$\frac{1}{ZP} = \frac{1}{z} [1 + \mu h + (\frac{1}{8}\mu^2 - \frac{1}{2})h^2 + (\frac{5}{2}\mu^3 - \frac{3}{2}\mu)h^3 + \&c.] \quad [\text{III.}]$$

$$= \frac{1}{z} (P_0 + P_1 h + P_2 h^2 + P_3 h^3 + \&c.). \quad [\text{IV.}]$$

Equation IV. is merely a simplified form of equation III., the expressions  $P_0, P_1, P_2, P_3$ , &c. being substituted for the coefficients of  $h^0$  or 1,  $h, h^2, h^3$ , &c. In the same way equation II. becomes

$$\frac{1}{ZP} = \frac{1}{a} (P_0 + P_1 h_1 + P_2 h_1^2 + P_3 h_1^3 + \&c.). \quad [\text{V.}]$$

The values of  $P_0, P_1, P_2$ , &c. can be readily seen from equation III. Below we write a few values which are determined from [III.].

$$P_0 = 1.$$

$$P_1 = \cos a \text{ or } \mu.$$

$$P_2 = \frac{3}{2}\mu^2 - \frac{1}{2}.$$

$$P_3 = \frac{5}{2}\mu^3 - \frac{3}{2}\mu.$$

$$P_4 = \frac{7}{2} \cdot \frac{5}{4}\mu^4 - \frac{5}{2} \cdot \frac{3}{2}\mu^2 + \frac{3}{2} \cdot \frac{1}{4}.$$

$$P_5 = \&c.$$

Equations [IV.] and [V.] are general expressions for the reciprocal of the distance, or  $\frac{1}{ZP}$ . We may therefore express

$$\frac{dS}{ZP} = \frac{dS}{z} \left( P_0 + P_1 \frac{a}{z} + P_2 \frac{a^2}{z^2} + \&c. + P_i \frac{a^i}{z^i} \right) \quad [\text{VI.}]$$

$$= \frac{dS}{a} \left( P_0 + P_1 \frac{z}{a} + P_2 \frac{z^2}{a^2} + \&c. + P_i \frac{z^i}{a^i} \right). \quad [\text{VII.}]$$

Equation VI. must be employed if  $z$  is greater than  $a$ , and [VII.] if  $z$  is less.

We made  $dS$  a small element of the portion of the spherical shell bounded by the coil.

In polar co-ordinates

$$dS = -a^2 d\mu d\phi;$$

$S$  will evidently be the integral of the above when  $\phi$  is integrated between the limits of 0 and  $2\pi$ , and  $\mu$  is integrated between  $\cos a$  and 1, or

$$S = 2\pi a^2 \int_{\mu}^1 d\mu.$$

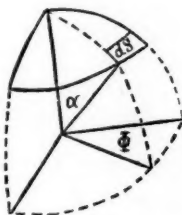


Fig. 3.

Hence the potential at  $Z$  due to the included shell is  $V = \frac{S}{ZP}$ , where  $ZP$  is the distance to each element of area of the sphere.

$$V = 2\pi a \left\{ \int_{\mu}^1 P_0 d\mu + \frac{z}{a} \int_{\mu}^1 P_1 d\mu + \&c. + \frac{z^i}{a^i} \int_{\mu}^1 P_i d\mu \right\}. \quad [\text{VIII.}]$$

$$V' = 2\pi \frac{a^2}{z} \left\{ \int_{\mu}^1 P_0 d\mu + \frac{a}{z} \int_{\mu}^1 P_1 d\mu + \&c. + \frac{a^i}{z^i} \int_{\mu}^1 P_i d\mu \right\}. \quad [\text{IX.}]$$



Substituting the value of  $V$  and  $V'$  from equations [XII.] and [XIII.] for  $V$  in the expression

$$\Omega = -\frac{1}{a} \frac{d(rV)}{dr},$$

and differentiating, we find

$$\Omega = -2\pi \left\{ 1 - \cos a + \&c. + \frac{\sin^2 a}{i} \frac{r^i}{a^i} \frac{dP_i(a)}{d \cos a} P_i(\theta) \right\}; \quad [\text{XIV.}]$$

$$\begin{aligned} \Omega' = 2\pi \sin^2 a \left\{ \frac{1}{2} \frac{a^2}{r^2} P_1(\theta) \frac{dP_1(a)}{d \cos a} + \&c. \right. \\ \left. + \frac{1}{i+1} \frac{a^{i+1}}{r^{i+1}} \frac{dP_i(a)}{d \cos a} P_i(\theta) \right\}. \quad [\text{XV.}] \end{aligned}$$

These are the most general expressions for the potential at any point whatever, due to a single coil of wire. Equation [XIV.] must be employed if  $r$  is less than  $a$ , or if the point lies within the sphere of which  $a$  is the radius and [XV.] for all points outside.

If the origin had been taken at the centre of the circular coil,  $a$  would have been equal to  $\frac{\pi}{2}$  or  $90^\circ$ . Substituting this value for  $a$  in [XIV.] and [XV.],

$$\Omega = -2\pi \left\{ 1 - \cos 90^\circ + \&c. + \frac{\sin^2 90^\circ}{i} \frac{r^i}{a^i} \frac{dP_i(90^\circ)}{d \cos 90^\circ} P_i(\theta) \right\};$$

$$\begin{aligned} \Omega' = 2\pi \sin^2 90^\circ \left\{ \frac{1}{2} \frac{a^2}{r^2} P_1(\theta) \frac{dP_1(90^\circ)}{d \cos 90^\circ} + \&c. \right. \\ \left. + \frac{1}{i+1} \frac{a^{i+1}}{r^{i+1}} \frac{dP_i(90^\circ)}{d \cos 90^\circ} P_i(\theta) \right\}. \end{aligned}$$

Noticing that  $\cos 90^\circ = 0$ , and that all the even orders of  $\frac{dP}{d \cos a}$  are multiplied by  $\cos a$ , and therefore equal to 0, we have

$$\begin{aligned} \Omega = -2\pi \left\{ 1 + \frac{r}{a} P_1(\theta) - \frac{1}{2} \frac{r^3}{a^3} P_3(\theta) \right. \\ \left. + \frac{3}{8} \frac{r^5}{a^5} P_5(\theta) - \frac{5}{16} \frac{r^7}{a^7} P_7(\theta) + \&c.; \right. \end{aligned}$$

$$\begin{aligned} \Omega' = 2\pi \left\{ \frac{1}{2} \frac{a^2}{r^2} P_1(\theta) - \frac{3}{8} \frac{a^4}{r^4} P_3(\theta) \right. \\ \left. + \frac{5}{16} \frac{a^6}{r^6} P_5(\theta) - \frac{35}{128} \frac{a^8}{r^8} P_7(\theta) + \&c. \right. \end{aligned}$$

We have heretofore supposed the coil to have been made of a single turn of wire. If the coil consists of a number of turns of wire, the

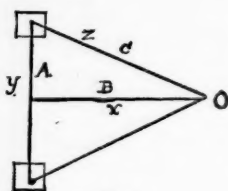


Fig. 5.

potential at any point may be obtained by the following approximation. Let the single turn, the potential due to which at any point we found could be expressed by equation [XIV.] or [XV.], occupy the centre of the coil whose rectangular dimensions are  $\xi$  and  $\eta$ . Let the co-ordinates of the wire at the centre of the coil be  $x$  and  $y$ . Now the potential at  $O$  due to the coils whose cross-

sectional area is  $\xi\eta$  will be a function of  $x$  and  $y$ . If we look at equation [XIV.],

$$\Omega = -2\pi + 2\pi \cos a - 2\pi \frac{\sin^2 a}{a} \frac{dP_1(a)}{d \cos a} r P_1(\theta) + \&c. \\ + 2\pi \frac{\sin^2 a}{ia^3} \frac{dP_i(a)}{d \cos a} r^i P_i(\theta), \quad [\text{XVI. A.}]$$

or, as it may be written,

$$\Omega = -2\pi + 2\pi Q_0 - 2\pi Q_1 r P_1(\theta) + \&c. + 2\pi Q_i r^i P_i(\theta), \quad [\text{XVI. B.}]$$

we see that  $Q_0$ ,  $Q_1$ ,  $Q_i$  &c. are such functions of  $x$  and  $y$ .

Let  $G$  be the mean value of  $Q$  for the values of  $Q$  for each wire within the limits  $+\frac{1}{2}\xi$ ,  $-\frac{1}{2}\xi$ ,  $+\frac{1}{2}\eta$ , and  $-\frac{1}{2}\eta$ , or

$$G = \frac{\int_{-\frac{1}{2}\xi}^{+\frac{1}{2}\xi} \int_{-\frac{1}{2}\eta}^{+\frac{1}{2}\eta} Q dx dy}{\xi \eta}. \quad [\text{XVII.}]$$

This expression gives the value of a new coefficient  $G$  for the coil whose cross-section is  $\xi\eta$  in place of  $Q$ , the coefficient for a single turn. From this we see that the potential at a point  $O$  due to the coil  $\xi\eta$  is

$$\Omega = -2\pi + 2\pi G_0 - 2\pi G_1 r P_1(\theta) + \&c. + 2\pi G_i r^i P_i(\theta); \quad [\text{XVIII.}]$$

or, calling  $G' = 2\pi G$ , we have

$$\Omega = -2\pi + G'_0 - G'_1 r P_1(\theta) + \&c. + G'_i r^i P_i(\theta). \quad [\text{XIX.}]$$

Expanding the numerator of equation [XVII.] by Taylor's theorem, integrating between the limits  $\frac{1}{2}\xi$ ,  $-\frac{1}{2}\xi$ ,  $\frac{1}{2}\eta$ ,  $-\frac{1}{2}\eta$ , and dividing by the denominator, we obtain a value for  $G$  of the form

$$G = Q + \frac{1}{24} \left( \xi^2 \frac{d^2 Q}{dx^2} + \eta^2 \frac{d^2 Q}{dy^2} \right) + \frac{1}{960} \left( \xi^4 \frac{d^4 Q}{dx^4} + \eta^4 \frac{d^4 Q}{dy^4} \right) + \&c. \text{ [XX.]}$$

This is the general expression for the values of  $G$ . To find  $G_0$ ,  $G_1$ , &c., we substitute the values of  $Q_0$ ,  $Q_1$ , &c., respectively, taken from equation [XVI. A]. Thus from a comparison of [XVI. A] and [XVI. B] we see that  $Q_0 = \cos a$ ; from Figure 5, we see that

$$\cos a = \frac{x}{z} = \frac{x}{\sqrt{x^2 + y^2}};$$

$$\frac{d^2}{dx^2} \left( \frac{x}{\sqrt{x^2 + y^2}} \right) = - \frac{3y^2 x}{(x^2 + y^2)^{\frac{5}{2}}};$$

$$\frac{d^2}{dy^2} \left( \frac{x}{\sqrt{x^2 + y^2}} \right) = \frac{2xy^2 - x^3}{(x^2 + y^2)^{\frac{5}{2}}}.$$

Substituting in equation [XX.], we find

$$G_0 = \frac{x}{z} \left\{ 1 + \frac{1}{24} \frac{2y^2 - x^2}{z^4} \xi^2 - \frac{1}{8} \frac{y^2}{z^4} \eta^2 \right\};$$

or, since  $G' = 2\pi G$ ,

$$G'_0 = 2\pi \frac{x}{z} \left\{ 1 + \frac{1}{24} \frac{2y^2 - x^2}{z^4} \xi^2 - \frac{1}{8} \frac{y^2}{z^4} \eta^2 \right\}.$$

$G'_1$ ,  $G'_2$ , &c. are found in the same way.

$$G'_1 = \frac{2\pi y^2}{z^3} \left\{ 1 + \frac{1}{24} \left( \frac{2}{y^2} - 15 \frac{x^2}{z^4} \right) \xi^2 + \frac{1}{8} \left( \frac{4x^2 - y^2}{z^4} \right) \eta^2 \right\};$$

[XXI. A.]

$$G'_2 = \frac{3\pi y^2 x}{z^5} \left\{ 1 + \frac{1}{24} \left( \frac{2}{y^2} - \frac{25}{z^2} + \frac{35y^2}{z^4} \right) \xi^2 + \frac{5}{24} \left( \frac{4x^2 - 3y^2}{z^4} \right) \eta^2 \right\};$$

$$G'_3 = \frac{4\pi}{z^7} \left( y^2 x^3 - \frac{y^4}{4} \right) + \frac{\pi \xi^2}{24 z^{11}} \{ z^4 (8x^2 - 12y^2) + 35x^2 y^2 (5y^2 - 4x^2) \} \\ + \frac{\pi \eta^2}{24 z^{11}} \{ 3y^2 z^2 (5y^2 - 44x^2) + 63x^2 y^2 (4x^2 - y^2) \}.$$

This same method of approximation may be applied to equation [XV.]:

$$\Omega' = 2\pi \frac{\sin^2 a}{2} \frac{a^2}{r^2} P_1(\theta) \frac{dP_1(a)}{d \cos a} + \&c. \\ + 2\pi \sin^2 a \frac{a^{i+1}}{i+1} \frac{1}{r^{i+1}} \frac{dP_i(a)}{d \cos a} P_i(\theta). \quad [\text{XV.}]$$

Substituting  $g$  for those terms depending upon  $x$  and  $y$ ,

$$\Omega' = 2\pi g_1 \frac{1}{r^2} P_1(\theta) + \&c. + 2\pi g_i \frac{1}{r^{i+1}} P_i(\theta), \quad [\text{XXI. B.}]$$

the value for one turn. Let  $g$  be the mean value for all the turns within the coil of cross-section  $\xi \eta$ , as deduced from the expression

$$g = q + \frac{1}{24} \left( \xi^2 \frac{d^2 q}{dx^2} + \eta^2 \frac{d^2 q}{dy^2} \right) + \&c.$$

Then, for the potential due to the whole coil,

$$\Omega' = 2\pi g_1 \frac{1}{r^2} P_1(\theta) + \&c. + 2\pi g_i \frac{1}{r^{i+1}} P_i(\theta);$$

or, calling  $g_1' = 2\pi g_1$ ,

$$\Omega' = g_1' \frac{1}{r^2} P_1(\theta) + g_2' \frac{1}{r^3} P_2(\theta) + \&c.; \quad [\text{XXII.}]$$

$$g_1 = \frac{\sin^2 a}{2} a^2 \frac{dP_1(a)}{d \cos a} = \frac{1}{2} \frac{y^2}{z^2} z^2 = \frac{1}{2} y^2;$$

$$g_1 = \frac{1}{2} y^2 + \frac{1}{24} \xi^2;$$

$$g_1' = \pi y^2 + \frac{1}{12} \pi \xi^2; \quad [\text{XXIII.}]$$

$$g_2' = 2\pi y^2 x + \frac{1}{6} \pi x \xi^2;$$

$$g_3' = 3\pi y^2 (x^2 - \frac{1}{4} y^2) + \frac{\pi}{8} \xi^2 (2x^2 - 3y^2) + \frac{\pi}{4} \eta^2 y^2.$$

Equations [XIX.] and [XXII.] give the value of the potential at any point due to the current in a coil of any shape.

If now, instead of finding the potential at a point, we wish to find the force exerted by two coils, the one upon the other, we may replace the point by a coil and calculate the mutual potential of the two coils from the formulæ already deduced. Let us suppose, at first, that the two coils are co-axial. Then we may replace the coils by spherical magnetic shells, which are concentric. The radius of the larger shell will be  $a_1$  and of the smaller  $a_2$ ;  $a_1$  and  $a_2$  will be the angular radius of the larger and smaller coils respectively. Let  $\Omega$  be the potential due to the first shell at any point within it, then the work required to carry the second shell to an infinite distance is given by the equation

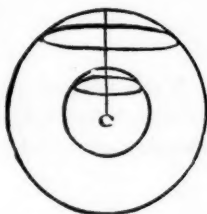


Fig. 6.

$$M = - \iint \frac{d\Omega}{dr} dS$$

(see Maxwell, § 423), extended over the smaller shell. Hence, since

$$\int dS = 2\pi a_2^2 \int_{\cos a_2}^1 d\cos \theta,$$

$$M = \int_{\cos a_2}^1 \frac{d\Omega}{dr} 2\pi a_2^2 d\cos \theta, \quad [\text{XXIV.}]$$

$\theta$  being the varying angular radius of the smaller coil.

In equation [XIV.]

$$\begin{aligned} \Omega = & -2\pi + 2\pi \cos a_1 - 2\pi \sin^2 a_1 \frac{r}{a_1} \frac{dP_1(a_1)}{d\cos a_1} P_1(\theta) + \&c. \\ & + 2\pi \frac{\sin^2 a_1}{i} \frac{r^i}{a_1^i} \frac{dP_i(a_1)}{d\cos a_1} P_i(\theta); \end{aligned}$$

differentiating  $\Omega$  with respect to  $r$ , and substituting in [XXIV.],

$$\begin{aligned} M = & 4\pi^2 \sin^2 a_1 a_2^2 \left[ \frac{1}{a_1} \frac{dP_1(a_1)}{d\cos a_1} \int_{\cos a_2}^1 P_1(\theta) d\cos \theta + \&c. \right. \\ & \left. + \frac{r^{i-1}}{a_1^i} \frac{dP_i(a_1)}{d\cos a_1} \int_{\cos a_2}^1 P_i(\theta) d\cos \theta \right]. \end{aligned}$$

Substituting the value of  $\int_{\cos a_2}^1 P(\theta) d\cos \theta$  from [IX. B] page 352, we find

$$M = 4\pi^2 \sin^2 a_1 \sin^2 a_2 a_2^2 \left[ \frac{1}{2a_1} \frac{dP_1(a_1)}{d\cos a_1} \frac{dP_1(a_2)}{d\cos a_2} + \&c. \right. \\ \left. + \frac{1}{i(i+1)} \frac{a_2^{i-1}}{a_1^i} \frac{dP_i(a_1)}{d\cos a_1} \frac{dP_i(a_2)}{d\cos a_2} \right]. \quad [\text{XXV.}]$$

If now the axes are inclined, making an angle  $\theta$  with each other, we have as before (page 352) only to introduce the  $P(\theta)$  of the corresponding order, and  $a_2$  in place of  $r$ , which gives

$$M = 4\pi^2 \sin^2 a_1 \sin^2 a_2 a_2^2 \left[ \frac{1}{2a_1} \frac{dP_1(a_1)}{d\cos a_1} \frac{dP_1(a_2)}{d\cos a_2} P_1(\theta) + \&c. \right. \\ \left. + \frac{1}{i(i+1)} \frac{a_2^{i-1}}{a_1^i} \frac{dP_i(a_1)}{d\cos a_1} \frac{dP_i(a_2)}{d\cos a_2} P_i(\theta) \right] \quad [\text{XXVI.}]$$

as the expression for the mutual action of two circular currents of unit strength, the axes of the coils making an angle  $\theta$  with each other at a point  $c$  distant  $a_1$  and  $a_2$  from the circumference.

It will be observed that equation [XXVI.] may be written

$$M = \left\{ 2\pi \sin^2 a_1 \frac{1}{a_1} \frac{dP_1(a_1)}{d\cos a_1} \right\} \left\{ \pi \sin^2 a_2 a_2^2 \frac{dP_1(a_2)}{d\cos a_2} \right\} P_1(\theta) + \&c. + \\ \left\{ 2\pi \frac{\sin^2 a_1}{i} \frac{1}{a_1^i} \frac{dP_i(a_1)}{d\cos a_1} \right\} \left\{ 2\pi \sin^2 a_2 \frac{a_2^{i+1}}{i+1} \frac{dP_i(a_2)}{d\cos a_2} \right\} P_i(\theta).$$

The quantity within the first pair of brackets is precisely what we made  $Q'_i$  equal to in equation [XVI.], and the second quantity is what we made  $q'_i$  equal to in [XXI. B]; therefore equation [XXVI.] may be written

$$M = Q'_1 q'_1 P_1(\theta) + \&c. + Q'_i q'_i P_i(\theta). \quad [\text{XXVII.}]$$

This is for one turn. If we have coils of a number of turns of wire whose sectional areas are  $\xi \eta$ , the  $Q'$  and  $q'$  will be replaced by the corresponding values of  $G'$  and  $g'$  as given in [XXI. A] and [XXIII.]. This gives the general expression for the mutual action of two coils in the form

$$M = G'_1 g'_1 P_1(\theta) + G'_2 g'_2 P_2(\theta) + \&c. + G'_i g'_i P_i(\theta). \quad [\text{XXVIII.}]$$

If now one of the coils is free to move, so that there will be a variation in  $\theta$ , the angle between the axes of the two coils, it is evident that the moment of the force tending to increase  $\theta$  or  $F$  is

$$F = \frac{dM}{d\theta}, \text{ or}$$

$$F = G_1' g_1' \frac{dP_1(\theta)}{d\theta} + G_2' g_2' \frac{dP_2(\theta)}{d\theta} + G_3' g_3' \frac{dP_3(\theta)}{d\theta} + \&c.$$

$$F = -G_1' g_1' \sin \theta - G_2' g_2' \sin \theta \frac{dP_2(\theta)}{d \cos \theta} - G_3' g_3' \sin \theta \frac{dP_3(\theta)}{d \cos \theta} + \&c.$$

$$F = -\sin \theta (G_1' g_1' + G_2' g_2' \frac{dP_2(\theta)}{d \cos \theta} + \&c.).$$

Here  $\theta$  is the angle between the axes of the coil; if we call  $\theta$  the angle between the planes of the coils, we have

$$F = \cos \theta (G_1' g_1' + G_2' g_2' \frac{dP_2(\theta)}{d \cos \theta} + \&c.). \quad [XXX.]$$

In all these equations  $G'$  is dependent upon the larger coil, and  $g'$  upon the smaller. This same expression holds good if the smaller coil is replaced by a magnet, provided suitable values be given to  $g'$ . Let the magnet be long and uniformly magnetized. Let  $2l$  be the length; then

$$g_1 = 2l; \quad g_2 = 0; \quad g_3 = -6l^3.$$

Take the case of a single coil galvanometer with a small magnetic needle; when the needle is at rest, the two couple are

$$FCm = HM \sin \theta;$$

substituting  $F$  from equation [XXX.], we have

$$Cm \cos \theta (G_1' g_1' + G_2' g_2' \frac{dP_2(\theta)}{d\theta} + \&c.) = HM \sin \theta;$$

or

$$C = \frac{HM}{m (G_1' g_1' + G_2' g_2' \frac{dP_2(\theta)}{d\theta} + \&c.)} \tan \theta;$$

$$\text{or } C = \frac{H M}{m g_1' (G_1' + \frac{G_2' g_2'}{g_1'} \frac{d P_2(\theta)}{d \theta} + \&c.)} \tan \theta;$$

since  $g_1' = 2 l$ ,  $m g_1' = M$ , and

$$C = \frac{H}{G_1' + \frac{G_2' g_2'}{g_1'} \frac{d P_2(\theta)}{d \theta} + \&c.} \tan \theta. \quad [\text{XXXI.}]$$

If the needle is at the centre of the coil  $z = y$ ,  $x = 0$ , and equations [XXI. A] become, if  $n$  equal the number of windings,

$$G_1' = \frac{2 \pi n}{y} \left( 1 + \frac{1}{12} \frac{\xi^2}{y^2} - \frac{5}{8} \frac{\eta^2}{y^2} \right);$$

$$G_2' = 0;$$

$$G_3' = -\frac{\pi n}{y^3} \left\{ 1 + \frac{1}{2} \frac{\xi^2}{y^2} - \frac{5}{8} \frac{\eta^2}{y^2} \right\};$$

$$G_4' = 0.$$

If we had but one turn, [XXXI.] would become

$$C = \frac{H y}{2 \pi} \tan \theta,$$

the ordinary equation for a galvanometer.

## XXIII.

ON THE CONDITIONS THAT DETERMINE THE  
LENGTH OF THE SPECTRUM.

BY AMOS E. DOLBEAR.

Communicated February 10, 1886.

PROFESSOR LANGLEY'S conclusion as to the absence in the sun's rays of wave lengths as long as those to be found in the moon's rays has been a surprise to many, who for theoretical reasons have thought it to be wellnigh certain that all possible wave lengths were to be found in the sun's rays.

The common implication is that, when a body is being heated, the shorter wave lengths that appear are simply added to those already present, so that the spectrum's length is in a manner proportional to the temperature of the radiating body. If that was so it is difficult to see how there could be economy in electric glow lamps by simply using higher potential. It might give more light, but if at the same time the lower so-called heat-waves were just as numerous and with greater amplitude, that is, if the visible waves were not in any way the representatives of the energy of the lower end of the spectrum, then the amount of light would be proportional to the amount of energy expended, which is not the case.

Instead of that it increases as the 3d power. This great increase of the visible waves is then at the expense of the lower end of the spectrum, and any measure of the length of the spectrum from such a source would probably show a marked decrease in the length of it between a low red and a white heat. This, too, is in accordance with molecular dynamics. If there be a gaseous volume of elastic molecules at any assigned temperature, the molecules collide and vibrate between impacts. Their rates of vibration must depend upon their molecular weight and elasticity, and similar molecules vibrate at equal rates. The characteristic wave lengths, or those by which a given gas may be identified, are produced by the vibrations between impacts, and the number of impacts per second will depend upon the gaseous density.

Suppose a body capable of vibrating  $a$  times per second for its fundamental be struck  $b$  times per second; then will its rate of vibrating be interfered with  $\frac{a}{b}$  times. If  $b$  be less than  $a$ , then will there be a certain number of these vibrations made per second. If  $b$  be equal to  $a$ , then after the first impact the body will vibrate in its own period with increasing amplitude and without interference. If  $b$  be greater than  $a$ , then will interferences take place in all phases of the vibrations, and the body will not make any characteristic vibrations. That is, its fundamental rate will be destroyed. If the body can vibrate in any harmonic series, some of these harmonics might be present associated with such irregular forced vibrations above its fundamental number, and a spectrum of such a body would consist of such shorter waves. It would apparently be moved towards the blue end. If then the light-giving molecules of the sun have either so short a free path, or the velocity between impacts is so great, as to insure that the number of impacts per second is comparable with the vibrating rate of the molecules, one ought to expect that the fundamentals would largely be destroyed, and therefore could have no representations in the spectrum, while a colder body like the moon, with a vastly less molecular velocity, might have an appreciably longer spectrum.

## XXIV.

## CONTRIBUTIONS TO AMERICAN BOTANY.

BY ASA GRAY.

Communicated March 13, 1886.

1. *A Revision of the North American Ranunculi.*

ALMOST half a century ago the North American species of *Ranunculus*, as then known, were hastily compiled for Torrey and Gray's Flora, with very little knowledge of original materials; and they have not been elaborated since. The following is a summary of a recent painstaking study of them.

§ 1. *BATRACHIUM*, DC. Although the European forms or species of this subgenus are numerous and difficult, only a few are known in North America, and these still need investigation.

We have among them a peculiar type, and our species may be presented in this form.

- \* Styles subulate, not longer than the ovary, introrsely stigmatose, sometimes for the whole length: petals deciduous.
- + Submersed foliage capillary-multifid, in this country no other seen except far north and west: carpel-receptacle hairy.

*R. CIRCINATUS*, Sibth. Known by its short and sessile leaves, of rigid texture, forming an orbicular circumscription at right angles with the stem. Here belongs *R. longirostris*, Godron, the original from St. Louis. Sibthorp's name is preferred to the slightly earlier *R. divaricatus*, which, as Hiern has made out, belongs to *R. aquatilis*, var. *trichophyllus*.

*R. AQUATILIS*, L., we should still keep as a collective species, with the Linnæan name; the type of Linnæus being the form *heterophyllus*. This occurs in British America, and from North Alaska to California; but not a single specimen is known from the Atlantic United States. Instead, we have everywhere

Var. *TRICHOPHYLLUS*, — to keep up the earliest and most used specific name for the whole series of forms, — with many subvarieties.

The more rigid leaved forms are commoner westward. In New England and New York occurs the opposite extreme, with soft and flaccid leaves, commonly with longer divisions, which collapse completely on being drawn out of the water. Among the several names which may be taken up for it, *R. flaccidus*, Pers., is probably the oldest, and *R. submersus*, Godron, the latest.

+ + No submersed dissected leaves: carpel-receptacle glabrous.

*R. HEDERACEUS*, L. Collected in the year 1870, by Mr. J. M. M. Muir, in fresh-water marshes at Norfolk, Virginia, said to be "apparently indigenous at many stations." But, as it nowhere else occurs, it was probably introduced from Europe.

\* \* Styles long and filiform, with small terminal stigma: receptacle glabrous: petals not deciduous: submersed leaves very few or none.

*R. LOBBII*, Hiern in Seem. Jour. Bot. ix. 66, t. 114, as subspecies. Hiern has in general well indicated the characters of this very rare species of California, and probably of Oregon, (which Torrey had referred to *R. hederaceus*, comparing it with *R. tripartitus*.) having noted the stamens as only 5 to 9, and the carpels as 4 to 6, with the "style slender, usually long and curved." He adds "lateral," which is not the case in the flower, nor indeed at a later period. But he did not perceive how completely distinct and peculiar this species is in its style of thrice the length of the ovary from which it abruptly proceeds, straight (not "curved"), of same thickness from base to apex, where it bears a small and wholly terminal stigma; also, that the few akenes are enclosed in the marcescent-persistent sepals quite to maturity. The style withers away, only its base remaining as a tip to the akene. So far as known, the California plant, of only Bigelow's collection, shows neither roots nor submersed leaves. I have not seen Lobb's plant, from Oregon, from which some filiform-dissected leaves are figured; and Bigelow's does not bear akenes with such strongly ascending and continuous lines on the faces of the akene as are shown in Hiern's fig. 9.

§ 2. *OXYGRAPHIS*. Sepals herbaceous and persistent: carpels utricular. — In view of the two following sections and the great diversity in the texture of the carpels in other parts of the genus, there is not much doubt that *Oxygraphis* of Bunge should be re-manded to *Ranunculus*. If the fruiting carpels are truly "a dorso compressa," the genus may perhaps be retained, since they seem to have a certain likeness to those of *Myosurus*, especially to those of

the American *M. apetalus*. That is, they are of rather firm texture on the back, which is produced into the still firmer beak, while they are ventrally thin and utricular, and either laterally somewhat flattened or turgid. In fact, the figure by Schlechtendal, in *Linnaea*, seems fairly to represent the general form of the carpel, notwithstanding Ledebour's note to the contrary. Prof. Oliver called my attention to the fact that they are in a measure follicular, being disposed to dehisce or burst open ventrally. I have shown (in Bull. Torrey Club for January, 1886) that this is rather strikingly the case in all the species of *Myosurus*, where, nearly the whole length of the body of the semi-utricular akene being attached to the rhachis, a rather obvious sutural dehiscence takes place, or is readily produced by slight pressure, when the fruit falls away. As restored to *Ranunculus* the species take their older names of *R. Kamtschaticus*, DC. (which may probably occur on the American side of the strait), and *R. polypetalus*, Royle. As to *O. Shaftoanus*, by some oversight the authors failed to notice its nearer relationship to *R. glacialis* and *R. Andersoni*, q. v.

§ 3. PSEUDAPHANOSTEMMA. Petals (reduced to a long-unguiculate nectary) and petaloid (white) tardily deciduous sepals of § *Aphanostemma*, with lanceolate utricular carpels nearly of *Oxygraphis*; these lanceolate, tapering into a slender style, thin-membranaceous throughout, compressed. Leaves round-reniform, 5-7-lobed and crenate-dentate.

R. HYSTRICULUS, Gray, Proc. Am. Acad. vii. 328. *Kumlieniahystriacula*, E. L. Greene, Bull. Calif. Acad. i. 337. Besides *Oxygraphis* there are certain New Zealand and Aucklandian *Ranunculi* which approach this in the character of the fruit.

§ 4. CRYMODES, i. e. *glacialis*. Petals (rose-color, white, or rarely yellow) ample, and with the sepals marcescent-persistent: carpels wholly or partly utricular, compressed and broad: showy-flowered perennials, chiefly arctic-alpine.

\* Akenes becoming partly coriaceous in age, and the scarious portion becoming a wing-like border, but still bilamellar and pervious.

R. GLACIALIS, L. Comes as near to our continent as Greenland.

R. CHAMISSONIS, Schlecht. Comes still nearer to our continent on the Asiatic side of Bering Strait. Akenes apparently more utricular and gibbous, and style longer than in *R. glacialis*, but little known.

\* \* Akenes wholly thin-utricular.

R. ANDERSONI, Gray, Proc. Am. Acad. vii. 327; Watson, Bot. King Exp. 6, t. 1. Habit and foliage nearly of the preceding.

R. SHAFTOANUS, *Oxygraphis Shaftoana*, Aitch. & Hemsl. in Jour. Linn. Soc. xix. 140, t. 3, of Afghanistan, is clearly a congener, with simply ternatisect, instead of triternatisect leaves.

§ 5. CYRTORHYNCHA (Benth. & Hook.), Gray, Proc. Acad. 1863, 56. Petals (yellow) bearing a prominent callosity instead of nectariferous pit and scale: carpels 10 to 18, *Thalictrum*-like, being terete and prominently about 10-costate, subcoriaceous and somewhat utricular, tipped with an *inflexed* style.

R. NUTTALLII, Gray, l. c. *Cyrtorhyncha ranunculina*, Nutt.

§ 6. HALODES. Like *Euranunculus*, but mature carpels thin-walled and utricular, the sides nervose: scapose and flagelliferous.— Here *R. plantaginifolius*, Murr. (*R. salsuginosus*, Pall.? DC., *R. Ruthenicus*, Jacq.) of Siberia, and the very widely diffused

R. CYMBALARIA, Pursh. Greenland, N. and Central Asia, the whole breadth of N. America, to extra-tropical S. America.

§ 7. EURANUNCULUS. Petals (with nectariferous pit and scale, usually yellow) and sepals deciduous: akenes crustaceous or firm-coriaceous, the sides nerveless, not transversely rugose.

\* Petals white, 8 to 10: sepals 3 or 4.

R. PALLASII, Schlecht. Alaskan Islands to Labrador fide *E. Martens*, but this needs confirmation. Lapland, Arctic E. Asia.

\* \* Petals in ours yellow, commonly 5, in a few species reduced to 3, in others increased to 6 or 8, or even 10 to 16.

+ Amphibious aquatic, with submersed foliage of § *Batrachium*.

R. MULTIFIDUS, Pursh, with its var. TERRESTRIS, and various intermediate forms. No one seems to know anything of the earlier homonym of Förskall, and so the present name seems by general consent to hold for the American species.

+ + Terrestrial and arctic-alpine perennials (or the first species rather amphibious and barely subalpine), creeping and fibrous-rooting, either from procumbent stems or from filiform rootstocks; the rounded leaves palmately 3-5-lobed or parted, but not divided nor filiform-dissected: flowers small.

++ Leafy-stemmed and rooting at the nodes, short-styled, and akenes in a globular head.

R. NATANS, C. A. Meyer. To this, rather than to *R. multifidus*, should be referred *R. radicans*, C. A. Meyer, and *R. Purshii* of Torr. in Ann. Lyc. N. Y. ii. 162.

R. HYPERBOREUS, Rothb.

++ ++ Scapose from filiform rootstocks, oligogynous, and long-styled.

R. LAPPONICUS, L.

+ + + Uliginous or subaquatic, fibrous-rooted, with entire or merely denticulate or crenulate and petiolate leaves.

++ Akenes beakless or nearly so, dull: subannuals, sometimes rooting from the lower nodes, but hardly thereby perennial.

= Petals 1 to 3 or 5, not over a line long: stamens 5 to 10.

R. TRACHYSPERMUS, Engelm. Pl. Lindh. i. 3, no. 2 (not Ell.), excl. var. *Lindheimeri*. Carpel-heads oblong or cylindraceous. — Louisiana and Texas.

R. PUSILLUS, Poir. — New York to Texas. *R. Bonariensis*, Poir. is very near to this, and of no older date. *R. fontanus*, Presl, of S. Italy, is also near, and perhaps was introduced from America.

Var. LINDHEIMERI. A small form, with akenes more papillose-roughish, but traces of this are not uncommon in *R. pusillus*. — *R. trachyspermus*? var. *Lindheimeri*, Engelm. Pl. Lindh. i. 3; Torr. Pacif. R. Rep. iv. 62. — Galveston, Texas, *Lindheimer*. California, in Napa Valley, *Bigelow*, and San Rafael, *J. P. Morse*, from *E. L. Greene*. Widely distant stations; but the plants seem to be specifically the same.

= = Petals 5, bright yellow, surpassing the calyx, 1 to 3 lines long: stamens numerous: style wholly deciduous.

R. OBLONGIFOLIUS, Ell. *R. pusillus*, var. *oblongifolius*, and *R. Flammula*, var. *laxicaulis*, Torr. & Gray, Fl. i. 16, 17. *R. Texensis*, Engelm. Pl. Lindh. i. 2. — Illinois and S. Carolina to Texas.

++ ++ Akenes subulate-beaked (but beak sometimes deciduous or reduced to an apiculation), in a globular head: petals 5 or more.

= Perennial by rooting from the nodes of creeping or the lower nodes of ascending stems, wholly fibrous-rooted.

R. HYDROCHAROIDES, Gray, Pl. Thurb. in Mem. Amer. Acad. v. 306. — S. Arizona, *Thurber*, *Capt. Smith*, *Rothrock*, *Lemmon*, to Southern California east of the Sierra, *Kellogg*. *R. stolonifer*, Hemsl., of Northern Mexico, is related to this, but is much smaller-flowered. Both have cordate lower leaves.

R. FLAMMULA, L., of which we have not the type, but only var. INTERMEDIUS, Hook. (from Lake Ontario to California and northward), and var. REPTANS, E. Meyer.

R. AMBIGENS, Watson, Proc. Am. Acad. xiv. 289, & Bibl. Ind. 16. *R. Flammula* & *R. Lingua* of Pursh, &c. *R. Flammula*, Torr. &

Gray, l. c., excl. var. *R. alismæfolius*, Benth. Pl. Hartw. 295, as to the Eastern plant only, & Gray, Man. 41, not Geyer. — Canada to Georgia. The American analogue of *R. Lingua*.

= = Strictly perennial, with thickened-fibrous and fascicled roots, terrestrial: stems short, erect or assurgent, not rooting from nodes above ground: mature akenes turgid, and with introrsely apical or subapical rather short subulate beak.

*R. ALISMÆFOLIUS*, Geyer, fide Benth. Pl. Hartw. 295, as to Geyer's original and the Hartweg plant, but not the Eastern species, as is well shown by Watson, Proc. Am. Acad. xix. 289. — Idaho to California. *R. Bolanderi*, Greene, Bull. Calif. Acad. ii. 58, answers to the type of this species.

Var. *ALISMELLUS*, Gray, Proc. Am. Acad. vii. 328, &c. The var. *montanus*, Watson, Bot. King, is partly this, partly a larger form which answers better to the robust type of the species. The Asiatic *R. Pseudo-Hirculus*, Schrenk, which I had collated to this, is quite different, and probably an entire-leaved form of *R. pulchellus*.

*R. LEMMONI*, Gray, Proc. Am. Acad. xi. 69. Has more turgid and villous-pubescent akenes in an oblong head; and the lower part of the low stem is often villous. It has been found only in Sierra Valley by its discoverer, *Lemmon*, and in S. Utah by *Siler*. Specimens of the preceding have been distributed under this name, leading to some confusion.

+ + + + Terrestrial species, with at least some lobed or divided leaves, and no stoloniferous rooting or creeping stems, except in *R. repens* and *R. septentrionalis*. Under this head the remaining species are disposed.

++ Calyx clothed externally with long and soft black or brown hairs: arctic-alpine and low perennials, with solitary large flowers, none with leaves divided to base.

*R. MACAULEYI*, Gray, Proc. Am. Acad. xv. 45. Roots a fascicle of fleshy fibres: leaves short-petioled, soft pilose or soon glabrous, thick, varying from almost linear with truncate 2-3-dentate apex to obovate-spatulate and obtusely 3-10-toothed: petals flabelliform, crenulate, mostly half-inch long, deep yellow. — Also published in U. S. Engineers' Report, 1878, p. 1883, Ruffner's Expl., as *R. nivalis*. — Alpine region of the Rocky Mountains in S. Colorado, at 11,700 feet, *Lieut. McCauley, Mr. Pease*. This is too near *R. Altaicus*, Laxm., which is *R. frigidus*, Willd. and Reichenb. Ic. Crit. iii. t. 289, and the *R. sulphureus* of some authors. Mature fruit is wanting.

*R. NIVALIS*, L. Extends across Arctic America, and from Hudson's Bay to the Alaskan Islands. A high arctic form, *R. sulphureus*, Solander in Phipps, &c., comes very near to *R. Altaicus*.

++ ++ Calyx not dark-hairy: akenes not muricate nor rough-hispid.

= Leaves some of them quite entire (except in the first species), some simply few-lobed and the lobes entire: alpine or subalpine low perennials, with fascicled-fibrous or tuberous roots, glabrous.

*a.* Radical leaves round-reniform and with 5 to 9 roundish lobes or deep crenatures: akenes dorsally carinate and subulate-beaked, collected in an oblong head.

*R. OXYNOTUS*, Gray, Proc. Am. Acad. x. 68. — Higher Sierra Nevada, *Brewer, Lemmon*.

*b.* Radical leaves neither reniform nor cordate, nor several-lobed: akenes turgid and dorsally rounded, collected in a globose head.

*R. GLABERRIMUS*, Hook. Fl. i. 12, t. 5. — Rocky Mountains to those of the Sierra Nevada and Brit. Columbia; early flowering. *R. brevicaulis*, Hook. Lond. Jour. Bot. vi. 66 (but not of the Flora) is a form of this.

*R. DIGITATUS*, Hook. Kew Jour. Bot. iii. 124, t. 4. Smaller, heterophyllous, 5-11-petalous; the roots fleshy-thickened in the manner of *R. Ficaria*. — Rocky Mountains, and west to those of Nevada and Utah.

= = Leaves all palmately or pedately lobed or divided, small: akenes turgid-lenticular, acute or acutish on the back, tipped with a small subulate beak: strictly arctic-alpine perennials, fibrous-rooted from a short caudex, tufted, a span or less high: flowers mostly solitary, not large, their rounded petals little surpassing the calyx.

*R. PYGMEUS*, Wahl. *R. Sabinii*, R. Br. — Throughout the breadth of Arctic America, and in the higher Rocky Mountains south to Colorado.

*R. HOOKERI*, Regel. Stouter: radical and often the very few cauline leaves biternately or pedately divided and parted, primary divisions sometimes petiolulate and the lobes linear-oblong or spatulate: stem 1-2-flowered: petals 3 lines long, surpassing the rounded sparsely and finely villous sepals: akenes a line long, in a globular head. — Pl. Radd. i. 47; Wats. Bibl. Ind. 19, not Schlecht. *R. pedatifidus*, Hook. Fl. i. 18, t. 6, not Smith, nor Schlecht. — Northern Rocky Mountains, *Drummond*. Gray's Peak, Colorado, *Patterson*, both in flower and fruit. The homonym of Schlechtendal is an extraordinary mixture,

and the Mexican plant, for which the name has by some been retained, has more than one earlier available name.

== = Leaves all 2-4-ternately parted or divided into numerous narrow divisions (of a line or less in width): akenes turgid, subulate-beaked, dorsally marginless, smooth and glabrous or nearly so: alpine or subalpine low perennials, with strong fibrous-fascicled roots, ascending stems and single or few large and showy flowers.

*R. TRITERNATUS*. Roots fleshy-fibrous: leaves usually triternately divided and parted; primary divisions long-petiolulate and lobes from filiform-linear to linear-spatulate, obtuse; petals broadly obovate (4 or 5 lines long): akenes very turgid, rounded dorsally, slender-beaked; the head globose, with a thick globular receptacle in the manner of *R. glaberrimus*. — Klikitat Co., Washington Terr., on high hills near Goldendale, *Howell*, by whom it has been distributed under the name of *R. Hookeri*. A very early-flowering and depressed form has broader radical leaves.

*R. ADONEUS*, Gray, Proc. Acad. Philad. 1863, 56, with syn. — High Rocky Mountains of Colorado and Utah; first coll. by Parry.

== == = Leaves mostly cleft or more divided, some rounded radical ones undivided, but at least crenate or dentate: akenes turgid or lenticular, marginless.

a. Montane or high northern, truly perennials: flowers with conspicuous and rather large petals, except in one form of *R. affinis*.

*R. ARIZONICUS*, Lemmon in herb. Gray. A foot or less high, glabrate or above glabrous, below usually with some soft villous hairs: fascicled roots thickish: stems slender and naked above, several-many-flowered: radical leaves round-cordate or sometimes cordate-oblong and strongly crenate-dentate, or later ones 3-7-cleft and segments 3-5-lobed; cauline once or twice 3-parted into narrow linear divisions: petals 5 to 7, oblong or obovate (3 to 5 lines long): akenes lenticular with thin and acute margins, lightly pubescent, commonly in a small globular head, having a subulate receptacle. — The plant sent by Mr. Lemmon with this name is the same as C. Wright's no. 837, also from S. Arizona, and which was taken for a form of *R. affinis* in the Botany of the Mexican Boundary. It grows in rather dry soil.

Var. *SUBAFFINIS*. Low, 1-few-flowered, like *R. affinis*, except the (equally pubescent) sharp-edged akenes, almost equalled by the subulate style. — Mt. Agassiz, *Lemmon*. A form from S. Arizona, *Rothrock*, connects with the following.

Var. *SUBSAGITTATUS*. Rather stout, decidedly villous, but the

pubescence deciduous: radical leaves mainly subcordate-oblong or obscurely sagittate, the middle nerves approximate: petals broadly obovate, half-inch long: akenes in a larger and oval head. — North Arizona in De la Vergne Park of the San Francisco Mountains, in wet ground, *Lemmon*.

**R. SUKSDORFII.** A span or less high, glabrous, 1-3-flowered: leaves small, somewhat reniform or flabelliform, 3-5-cleft or parted, divisions of the radical ones 3-5-cleft or incised, of the cauline linear: petals round-obovate, retuse, a third to half an inch long, deep yellow: akenes glabrous, turgid-lenticular, acutish-edged, surmounted by a nearly filiform style of equal length (three fourths of a line), which is apparently deciduous in age. — Mount Adams, Washington Terr., at 6,000 to 7,000 feet, in damp ground, *Suksdorf*.

2. Heads of carpels in fruit oblong or cylindraceous; akenes more turgid, rounded or at least obtuse on the back.

**R. ESCHSCHOLTZII**, Schlecht. This species has somewhat singularly been referred to *R. nivalis*, but its nearest relative is *R. affinis*. It has a much longer, slender-subulate, and mostly straight style.

**R. AFFINIS**, R. Br., has a small and mostly recurved style, much shorter than the ovary, at most only a quarter of the length of the akene, and often its thickish base only persists at maturity. These characters and the globular akenes well distinguish it from *R. auricomus*, L., of the Old World, to which some have referred it.

**Var. VALIDUS.** Taking the slender high-northern form with even the radical leaves sometimes "pedately multifid" as the original of the species, the above name may be given generally to the stouter and larger forms, of lower latitudes or elevation, with more succulent leaves, the radical mostly undivided and roundish, either cordate or truncate or cuneate at base, and from coarsely crenate to 3-7-cleft or parted, some later ones occasionally divided and even with the divisions petiolulate. To this belongs *R. cardiophyllus*, Hook., figured both in the Fl. Bor.-Am. and in Bot. Mag. t. 2999, but with the style too long.

3. Head of carpels in fruit globose; styles minute and straight.

**R. RHOMBOIDEUS**, Raf. Prec. Decouv. 36? & Goldie in Edinb. Phil. Jour. t. 11, f. 1; Hook., etc. As Rafinesque gives the habitat "Canada and Genessee," we may well suppose this was his plant; otherwise, his must remain wholly obscure. *R. brevicaulis*, Hook. Fl. i. 13, t. 7, is evidently a much depressed form of this species; and here also may be referred *R. auricomus*, var. *Cassubicus*, E. Meyer, Pl. Labrad. 96.

b. Pacific-coast species, large-flowered, long-styled, perennial.

R. BLOOMERI, Watson, Bot. Calif. ii. 426; found only in low grounds on San Francisco Bay. To this well-marked species may probably be referred *R. Chilensis*, Hook. & Arn. Bot. Beech. 134.

c. Chiefly Eastern N. American or cosmopolite, small-flowered, very short-styled; with compressed and small very short-beaked or beakless akenes, and slender-fibrous roots: biennial, or short-lived perennial, or, at least in the second species, annual.

R. ABORTIVUS, L., which passes freely into var. *micranthus*, Gray, Man. 42 (*R. micranthus*, Nutt., with hairy stems and some divided root-leaves), not smaller-flowered than the type. Connects with

Var. HARVEYI, which produces conspicuous petals, even 3 lines long, and very much surpassing the calyx. — On damp rocks in Arkansas, *F. L. Harvey* and *Dr. Hass*.

R. SCELERATUS, L. In the Eastern United States this has the look of an introduced plant, but doubtless indigenous in the interior, where it has a wide range.

===== Leaves variously cleft or divided: akenes compressed, generally flat, surrounded by a firm or indurated margin: none truly alpine or arctic.

a. Perennials with globular or ovoid carpel-heads (*R. Pennsylvanicus* and perhaps *R. hispidus* excepted), the akenes smooth or in some barely pubescent: mostly fibrous-rooted.

1. *Hook-styled*; the long styles recurving (at least in age) and wholly persistent in a rigid and uncinate elongated beak: petals only 5: stems erect: radical leaves hardly ever divided into separate leaflets. — *Oncostyli*, Gray, Proc. Am. Acad. viii. 373, excl. spec. 1.

R. RECURVATUS, Poir. Petals reflexed with and shorter or hardly longer than the reflexed calyx: akenes glabrous, but their receptacle hairy. — *R. lanuginosus*, Spreng., not Poir. *R. saniculæformis*, Muhl. *R. tomentosus*, Spreng., not Poir. — An Eastern species, extending westward to the Lake of the Woods.

R. OCCIDENTALIS, Nutt. To this wholly Western species — widely ranging geographically and in diversity — I am now constrained to join *R. Nelsonii*, Gray, Proc. Am. Acad. viii. 374 (*R. recurvatus*, var. *Nelsoni*, DC. Syst. i. 290); indeed, Nuttall's plant, now known in better original specimens, proves to be essentially that which I had taken as the type of *R. Nelsonii*. It is also, I believe, *R. Schlechtendalii*, Hook., Fl. i. 21 (although the fruit of that is unknown), as to the

specimens described, but not the plant of Schlechtendal which furnished the name, and which therefore would be the type of Hooker's species; wherefore his name would not supersede Nuttall's for the present species. The carpel-receptacle is naked and glabrous, and so not rarely are the akenes; but these, at least when young, are apt to bear some scattered and bristly hairs, especially along the dorsal margin, or also on the faces. The extreme forms, — very widely different in appearance, — as now regarded, are

**Var. ROBUSTUS.** A span to a foot or more in height, stout-stemmed and ample-leaved, large-flowered; the obovate petals 5 or 6 lines long; and carpels even 2 lines long, numerous in the head. — *R. occidentalis*, Gray, Proc. Am. Acad. viii. 374. *R. n. sp. forma prima, flores magni*, Schlecht. Animad. Ranunc. ii. 28, under *R. recurvatus*. — Chiefly Alaskan.

**Var. LYALLI** has rather large and thin leaves, short peduncles, and petals not longer than the calyx, — in all these points so much like *R. recurvatus* that it might be taken for a Western form of that species; but the carpel-receptacle is glabrous and the carpels themselves sparsely hispid with the peculiar bristly hairs of the present species. Lyall's specimens are from Pend Oreille River, in Idaho. But a similar form is found on the Oregon, near Portland, by *Howell*, where it passes evidently into the following.

**Var. TENELLUS.** Slender, sometimes tall and stems with long internodes, often glabrate: leaves simpler and smaller: flowers small: petals commonly oblong, paler, only 2 or 3 lines long: akenes fewer in the small heads, sometimes very few: styles, as in the preceding forms, persistent as a stout and flattened-subulate hooked beak and equalling or somewhat shorter than the akene; this either glabrous or bristly. — *R. tenellus*, Nutt. in Torr. & Gray. *R. Nelsonii*, var. *tenellus*, Gray, Proc. Am. Acad. viii. 374. *R. forma secunda*, Schlecht. l. c.? — In wet and shady woods, and "flowering as a winter-annual" (*Howell*), whence probably its slenderness.

**Var. EISENI.** More or less slender: petals 2 or 3 or even 4 lines long: akenes glabrous, with a beak of only about half their own length. — *R. canus*, Torr. Pacif. R. Rep. iv. 62, not Benth. *R. Eisenii*, Kellogg, Proc. Calif. Acad. vii. 115. — Sierra Nevada, California, to the Columbia River.

**Var. RATTANI.** Differs from the last variety only in the akenes, which become roughish-papillose, and are sparsely or thickly beset with short hairs; the strongly curved beak sometimes much and sometimes little shorter than the body of the akene. — N. California, on the

Klamath, *Rattan*, and adjacent Oregon, in Josephine Co., *Howell*; the latter a transition toward the typical *R. occidentalis*.

2. *Broad-hook-styled*, i. e. the recurved uncinat styles shorter than the ovary, broad and flat, stigmatose for most of their length, wholly persistent in a very strong and flat triangular or gladiate and hooked or curved beak which is much shorter than the flat akene: and confluent with its sharp margin: radical leaves divided or nearly so: petals only 5.

*R. ACRIFORMIS*. A foot high, strict, with pubescence in good part appressed: leaves all palmately or pedately and deeply 3-5-parted or even divided, and often again 2-3-cleft into narrower lanceolate or linear segments and lobes: petals orbicular-obovate, one fourth inch long, hardly double the length of the spreading calyx: akenes over a line long; beak of half their length. — *R. acris*, Hook. Fl. i. 18, partly, & Lond. Jour. Bot. vi. 66, not L. — Northern Rocky Mountains, lat. 58°, *Drummond*. Wyoming, *Parry* (distrib. as *R. affinis*). Wind River, *Dr. Forwood*, and near Cheyenne, *Greene*.

*R. CANUS*, Benth. Erect and robust, soon declining, densely soft-villous with white hairs when young, becoming greener and sparsely villous or glabrate: leaves or most of them 3-divided, and the middle or all three leaflets petiolulate, commonly cuneate and 2-3-cleft, with the lobes incised; petals obovate, half-inch or less in length, fully double the length of the soft-villous reflexed calyx: akenes  $2\frac{1}{2}$  to 3 lines long, the very broad beak less than a line long, forming part of the margin. — Pl. Hartw. 295. *R. Californicus*, var. *canus*, Brewer & Watson, Bot. Calif. i. 8. *R. occidentalis*, var., Gray, Proc. Am. Acad. viii. 374. — Low ground in the valley of the Sacramento, *Hartweg*, in flower only, but the hooked styles discerned by Bentham. Near Chico, *Mrs. Bidwell*, specimens just received in flower and fruit, from the district where Hartweg found it, enabling the completion of the character. There are other specimens from the region, in blossom only, which may belong to this species. The name is appropriate only to Hartweg's specimens; the white and soft pubescence being conspicuous only on the early growth.

3. *Short-styled*; the introrsely stigmatic styles thickish-subulate and mostly all persisting in the short (straight or recurved or even hooked) beak: herbage hirsute or pubescent.
- o Lax or weak-stemmed, Californian: no stolons: petals (rarely 5?) 6 to 15: beak of akenes stout-subulate, more or less hooked.

*R. CALIFORNICUS*, Benth. *R. dissectus*, Hook. & Arn. *R. del-*

*phnifolius*? Torr. & Gray, not Hook. The typical form narrow-leaved, but passing freely into

Var. *LATILOBUS*, a common coarse-leaved and more robust form. *R. Ludovicianus*, Greene, Bull. Calif. Acad. ii. 58.

o o Strictly erect species, nat. from Europe: no stolons: very short styles stigmatic for all or most of their length: petals 5, broad.

*R. ACRIS*, L. Possibly native in Newfoundland, as it is thought to be in Greenland.

*R. BULBOSUS*. Sparingly naturalized in most of the Eastern Atlantic States, copiously so in Eastern New England.

o o o Erect or ascending, not stoloniferous, 5-petalous: stout subulate style stigmatose for much of its length, persisting in a straight or merely oblique beak: roots fibrous, of short duration.

*R. PENNSYLVANICUS*, L. f. Well marked by its stout and tall upright leafy stem, annual or subannual root, rough-hirsute and widely spreading pubescence, ternately dissected leaves with petiolulate leaflets, petals not surpassing the reflexed calyx, and spicate (oblong or cylindraceous) head of short-beaked akenes.

*R. HISPIDUS*, Michx., partly, DC., Hook. Ascending or declined, usually but not always hispidly hirsute with spreading hairs, annual or biennial, or sometimes perhaps more enduring (the fascicled roots either slender or thickening): stems few-leaved, when reclining rarely if ever rooting: leaves all ternately compound: leaflets mostly slender-petiolulate in the manner of the preceding species, and of similar subdivision: peduncles rather long: petals obovate, mostly 3 lines long, surpassing the spreading or hardly reflexed and early deciduous calyx: akenes mostly a line and a half long, and with stout and straight (about half a line long) beak formed of the whole flat subulate style: head globular or at most oval. — Has been confounded with the preceding species, to which it is most related, and with *R. septentrionalis*, as well as with the true *R. repens*. But it has not the truly perennial roots of either, nor has it the creeping stolons of the one or the slender-tipped styles of the other. This is a Northern and Western species, extending from Canada to the Pacific coast and south to Colorado and Utah. The character "*stylo brevissimo*" marks it as the plant which De Candolle took up in Michaux's herbarium, and that probably came from Canada, while the other specimen, which De Candolle described as his *R. Carolinianus*, would be the one to which Michaux's habitat "*Carolinæ Inferioris*" belongs. We therefore cite *R. hispidus*, Michaux, Fl. i. 321, partly; DC. Syst. i. 289; Hook. Fl.

i. 19. The specific name is generally appropriate, but on the Pacific coast there is a smoothish or smooth form, viz. : —

Var. OREGANUS. Lucidulous, and with only scattered hairs, or sometimes hardly any. — *R. nitidus*, in part, Hook. Fl. i. 20. — Shady and wet grounds, Oregon, on the Columbia, to Fraser River. I use the name which Messrs. Howell and Henderson have proposed for this as a species.

- o o o o Ascending, also creeping by procumbent rooting branches or stolons: short-subulate styles stigmatose for the whole length, and all or nearly all persistent in the beak: principal leaves of ovate or roundish outline, not rarely white-variegated or spotted above, some only 3-parted, some divided, and with the middle lobe petiolulate; lateral ones either petiolulate or sessile.

*R. REPENS*, L., and partly so of American authors. — Low grounds, Nova Scotia and Canada to Virginia, New Mexico, &c., generally only in waste grounds near the coast, where it is naturalized from Europe, but also indigenous in some places. Here belongs *R. Clintonii*, Beck, Bot. 9, doubtless an introduced plant.

- 3. *Long-styled* and mostly long-beaked, i. e. styles more or less elongated and attenuate upward, stigmatose only at or near the tip, sometimes all persistent, more commonly with the slender upper part deciduous or at length breaking away from the basal, which remains as a beak: perennials.
- o Petals 5: primary radical leaves or some of them (at least in dry soil) commonly undivided and only 3-parted, but succeeding ones 3-5-foliolate.

*R. SEPTENTRIONALIS*, Poir. This I take to include the greater part of the assemblage of forms which have passed for *R. repens* in this country. It includes *R. septentrionalis*, *Marilandicus*, *tomentosus* (hairy form), *lucidus* (glabrous form), and *repens*, var. of Poir, Dict. vi. 112-127: also *R. hispidus*, Michx., as to the Southern plant upon which was founded *R. Carolinianus*, DC.; *R. nitidus*, Muhl., not Walt.; *R. Belvisii*, DC.; *R. palmatus*, Ell.; *R. fascicularis*, Schlecht. Animad. Ranunc. ii. 30, t. 2, (not truly of Muhl.,) therefore the *R. Schlechtendalii*, Hook. as to type; and *R. intermedius*, Eaton. *R. Philonotis* and *R. lanuginosus* of Pursh are probably of this species, mistakenly named. The species ranges from New Brunswick to Manitoba and south to Texas. In wet ground some summer stems are procumbent or sarmentose, and these occasionally strike root at the nodes.

*R. FASCICULARIS*, Muhl. (Cat. 54), Bigel. Fl. Bost. ed. 1, 137; Hook. Fl. i. 20, t. 8; Gray. Gen. Ill. i. t. 9. Known by its dwarf and tufted habit, tuberous-thickened roots, mostly appressed pubescence, and the disposition to pinnate or quinate division of the principal leaves; the style and beak longer, and the lenticular akenes less margined. — Canada and E. New England to Texas, and northwest to Winnipeg; flowering early.

o o Petals 7 to 16: no creeping nor procumbent basal stems.

*R. MACRANTHUS*, Scheele in Linnæa, xxi. 685. Hirsute: stems erect and a foot or two high, or 2 to 3 feet long and declining, commonly robust: leaves nearly as of *R. septentrionalis*, but many quinate: petals from a third to nearly a full inch long, from obovate to oblong: akenes mostly numerous in a large head, ovate or orbicular, conspicuously thin-edged, at length with a rather short and broad flat-subulate beak, the slender upper portion of the long and straight style falling away. — *R. repens*, var. *macranthus*, Gray, Pl. Lindh. i. 141, & Pl. Wright. — Low ground, Texas to S. W. Arizona, first coll. by Wright and Lindheimer.

*R. ORTHORHYNCHUS*, Hook. From hirsute to nearly glabrous: stems erect, a foot or two high from a fascicled root of thick fibres: leaves mostly of oblong outline and pinnate division into 5 or 7 leaflets or segments, these again usually cleft or incised: petals a third to half inch long, obovate, much surpassing the reflexed soon deciduous calyx: akenes usually not numerous in the head, ovate, nearly two lines long, strongly margined, bearing a slender-subulate rigid and quite straight beak of about the same length, consisting of the wholly persistent style. — Wonderfully various in foliage: the typical form, *STENOPHYLLUS*, has all the leaves somewhat bipinnately dissected into segments of a line or less in width, or some radical ones simply divided into cuneate or obovate 2-3-lobed or toothed segments or leaflets. — *R. orthorhynchus*, Hook. Fl. i. 21, t. 9. *R. dichotomus*, Schlecht. in Linnæa, vi. 579, but not the Mexican species. — Wet ground, W. Oregon and British Columbia. Passes freely into

Var. *PLATYPHYLLUS*. Robust, commonly large, sometimes 2 to 4 feet high, and leaves with limb 2 to 4 inches long; the ample segments or leaflets 1 to 3 inches long, from oblong or rhomboidal to ovate, laciniately cleft or incised: petals from a quarter to three quarters of an inch long. — *R. macranthus*, Watson, Bot. King Exped. & Bot. Calif., not Scheele. — In wet places, Wahsatch Mountains and Idaho to E. Oregon, and California, south to Marin Co.

b. Annuals or biennials, all but one introduced from the Old World.

1. Akenes smooth and even, or at length sprinkled with some scattered papillæ, especially toward the margin: flowers moderately large and showy.

*R. PARVULUS*, L. Certainly this was not a happy name since, like all such annuals, it may vary from depauperate to robust. One perhaps might follow the majority of authors in superseding it, if they had at all agreed as to what name they would adopt in its place. The oldest after the Linnæan is *R. Sardous*, Crantz; next is *R. hirsutus*, Curtis; then *R. Philonotis*, Retz; and the oldest name after the Linnæan is the one least used. The species is very sparingly naturalized in N. America, in the vicinity of some Atlantic seaports.

2. Akenes papillose-scabrous, and hispidulous with hooked hairs: flowers very small: indigenous to the Pacific coast.

*R. HEBECARPUS*, Hook. & Arn. Indigenous analogue of *R. parviflorus*.

3. Akenes muricate or echinate: sparingly naturalized.

*R. PARVIFLORUS*, L. Very small-flowered: akenes rough-papillose.

*R. MURICATUS*, L. Large-flowered, broad-leaved: akenes strong-beaked, tuberculate or echinate.

*R. ARVENSIS*, L., has effected a precarious lodgment only in some ballast grounds: it has narrow-lobed leaves and strongly echinate akenes.

## 2. *Sertum Chihuahuense*.

Next in interest to our own botany is that of the northern part of Mexico adjacent to the United States, and especially that of the elevated interior region. Two collections have been made (for the most part in sufficient numbers for distribution) during the past year, in the Mexican State of Chihuahua; one by Mr. C. G. Pringle, along the line of the Mexican Central Railway, in the spring and in the autumn of 1885; the other by Dr. Edward Palmer, from August to November of the same year, in the Sierra Madre of the southwestern part of that State, with headquarters at the mining settlement of Batopilas, in some maps printed Batopolas. Both are collectors of experience in adjacent regions, particularly in Arizona, whence Mr. Pringle had in former years penetrated into Sonora, very beneficially for botany, but to the damage of his own health; Dr. Palmer had made two

important explorations in more eastward Mexican States, one in the year 1878, in connection with Dr. Parry, with headquarters at San Luis Potosi, the other in 1879 and 1880, in Nuevo Leon and Coahuila. Mr. Pringle is now returning to this promising field, making the town of Chihuahua his starting point, and with the hope of passing the summer in the Sierra Madre lying to the west of that place.

Having now determined the *Gamopetalæ* of these two collections of 1885, I here bring together some account of the new and otherwise noteworthy species. The numbers following the name of the collector are those under which the specimens are distributed. The specimens of Mr. Pringle's distribution are accompanied by full printed tickets.

#### *Rubiaceæ.*

COUTAREA LATIFLORA, DC. Prodr. iv. 350. "A large shrub, about ten feet high, rather compact, with several stems and very green leaves: in the cañons and mountains above Batopilas," Palmer, *H.* Called "Copalquin," and the bark much used as a substitute for quinine, &c., according to Dr. Palmer. The specimens are in fruit only, the long and narrow calyx-lobes marcescent on the younger fruits. They answer well to the figure of Mocino and Sessé, even to the "tuberculis sparsis" on the capsule, although these slightly-raised and light-colored spots, as well as the ribs, are exaggerated in the rude sketches. The seeds are as represented, and very broadly winged. The popular name, as recorded by Dr. Palmer, nearly agrees with the "Copalchi" of the Prodomus.

HOUSTONIA POLYPREMOIDES. *Ereicotis*, *H. acerosæ* maxime affinis, at parum fruticulosa, laxius ramosa, spithamæa; foliis setaceo-subulatis minus crebris; floribus plerumque pedunculatis; corollæ (lin. 4 longæ) tubo calycem paullo superante. — Santa Eulalia Mountains, near Chihuahua, on gravelly limestone slopes. Corolla "white, changing to purple." Pringle, 16 and 356.

RANDIA PRINGLEI. Inermis; foliis ovalibus pube molli densa subcinereis subtus reticulatis basi in petiolum marginatum contractis; stipulis parvulis triangulari-subulatis; floribus in glomerulos sessiles terminales vel in axillis summis congestis; calycis lobis subulatis tubo supra ovarium crateriformi longioribus; corolla hypocraterimorpha; tubo extus puberulo vix semipollicari lobis ovatis acuminatis parum longioribus; styli ramis brevibus discretis sursum incrassatis truncatis; ovarii biloculari, placentis in axi leviter connatis; fructu fide Pringle vetustate globoso pollicari, pericarpio fragili seminibus planis farcto.

— In cañons of the mountains near Jimulco, S. W. Coahuila. "A spreading shrub or low-branched small tree, with creamy-white and fragrant flowers." *Pringle*, 142.

GENIPA ECHINOCARPA. *Randia echinocarpa*, DC. Prodr. iv. 385, and in Moçino & Sessé, Ic. ined. t. 469. "Called *Papache*. Shrub or small tree, 6 to 10 feet high, with sharp thorns; its numerous fruit covered with fleshy protuberances, of a dark green color outside; when ripe the inside is black, is much eaten, ripens in winter." — At the hacienda San Miguel, near Batopilas, *Palmer*, A. The dried fruit sent is firm-corticate, 2 inches in diameter, resembles the published tracing, except that a good number of the fleshy tubercles have developed into soft spines of nearly half an inch in length. The seeds, imbedded in the pulp, are not well preserved, but are flat and orbicular, and seem to be those of a *Genipa*; and there is no dissepiment. The spines of the branches are those of a *Randia*. Dr. Palmer sent no flowers. But I judge from the foliage that the flowering specimens of *Ervendberg's* collection at the settlement of War-tenberg, near Tantoyuca, distributed as "no. 239, *Randia*," may be the same; that has a one-celled ovary, and subulate calyx-lobes.

MACHAONIA, Humb. & Bonpl. § PLATTANTHEA. Corolla tubo vix ullo fauce concava fere rotata. Spec. 2:—

MACHAONIA FASCICULATA, Gray, Proc. Am. Acad. xix. 77. Micropphylla; foliis in axillis fasciculatis parvis subspathulatis. — Mexico, Coulter, no. 1167.

MACHAONIA PRINGLEI. Inermis: foliis (haud fasciculatis) lanceolatis utrinque acutis vel acuminatis subpetiolatis fere eveniis glaberrimis (1-2-pollicaribus); cymis laxe floribundis; floribus 4-5-meris; corollæ (albæ) lobis margine tenuiter undulatis. — S. W. Coahuila, on limestone ledges of the mountains near Jimulco, April, in flower: "a shrub 3 to 6 feet high," *Pringle*, 146. The funiculus from the summit of the cell is attached to the oblong-linear ovule about half-way between its middle and the micropyle.

MITRACARPUS VILLOSUS, Cham. & Schlecht. in Linn. iii. 363 (name by implication), & DC. Prodr. iv. 572 (fairly similar to the W. Indian plant); Hemsl. Biol. Centr.-Am. Bot. ii. 61. Near Batopilas, *Palmer*, 38. Includes the plant of *Berlandier* which has been referred to *M. breviflorum*. Differs from that in pubescence, though not enough to merit the specific name, in more evident venation, and in bearing bristly hairs along the margins of the sepals, but not so strikingly as in *Jacquin's* figure. For the reason of a return to the original orthography of the generic name, see *Syn. Fl. N. Am.* ii. 32.

CRUSEA SUBULATA, Gray, Proc. Am. Acad. xix. (not Hemsl., which is an error for *C. subulata*, Hook. & Arn.), the *Borreria subulata*, DC., a common Mexican species, was collected both by *Pringle*, 314, and by *Palmer*, 423.

CRUSEA PALMERI. *C. Wrightii* similis, pariter annua gracilisque, ultrapedalis, sed puberula tantum; foliis angusto-lanceolatis; floribus brevissime pedicellatis, pedicello cum ovario didymo glabro nudo; calyce fere *C. parvifloræ*, Hook. & Arn., extus hirsuto, lobis latiusculis mucronatis; corolla albida infundibuliformi calycem vix dimidio superante, lobis ovatis sub apice uni-pauci-setiferis antheris æquilongis. — Shaded hillsides, about 25 miles south of Batopilas and at much less elevation, *Palmer*, 70.

SPERMACOCE MEGALOCARPA. *S. lævigata* ut videtur affinis, subpedalis e radice annua brachiato-ramosa, glabra; foliis ovatis oblongisve acuminatis membranaceis (1-2-pollicaribus) pinnato-nervosis, inferioribus longe subalato-petiolatis, summis basi contracta subsessilibus capitulum laxum involuerantibus; vagina stipularum scariosa truncata setis paucis mollibus instructa rariusve nuda; floribus in pleris axillis perpaucis, in capitulo terminali sat numerosis; corolla styloque ignota (cito decidua): fructu ovali (lin. 3-4 longo) lævi coriaceo calycis lobis 4 filiformibus patentissimis mollibus ipso sæpe æquilongis superatis in carpella duo demum secedente, dissepimento tenui lato relinquirente; semine elongato-oblongo. — Wet places in the higher mountains above Batopilas, *Palmer*, 185. With mature fruit and apparently young flowers, having also a fusiform ovary surmounted by the narrow linear calyx-lobes; but even in the youngest not a trace of corolla or genitalia to be found. We have no *Spermacoce* of this habit, yet the fruit answers to the *Borreria* section of that genus.

#### *Compositæ.*

VERNONIA (EREMOSIS) STEETZII, Schultz Bip. in Seem. Bot. Herald, 297; a form with more slender heads. Ravines at the Frailes, half-way between Batopilas and the summit of the mountains, at about 7,000 feet. Stems herbaceous, "about 5 feet high," *Palmer*, 273.

STEVIA STENOPHYLLA, Gray, Proc. Am. Acad. xv. 25. This species has now been collected, on shaded cliffs near Chihuahua, by *Pringle*, 677.

STEVIA SALICIFOLIA, Cav. Low forms with aristate pappus, and thinner leaves than usual, with now and then some coarse teeth. Higher mountains near Batopilas, *Palmer*, 278, 391. And the var.

*nana*, Gray, l. c., was found near Chihuahua, by *Pringle*, 677 $\frac{1}{2}$ , 102.

**STEVIA VENOSA.** *S. Plummeræ*, Gray, et *S. scabrellæ*, Benth. sat affinis, glabra, foliosa; caulibus ut videtur omnino herbaceis ultrapetalibus; foliis subsessilibus subcoriaceis (1-2-pollicaribus) fere integerrimis oblongo-lanceolatis acutis tripli- vel tri-nerviis venosis, venis prominulis adscendentibus laxè reticulatis modo *S. Plummeræ*; cymis compactis fastigiatis; pedicellis brevissimis; involucrio vix lin. 3 longo sæpius 4-floro parum viscidulo-puberulo, bracteis obtusis; floribus saturate purpureis; pappo coroniformi brevi subcoriaceo margine eroso. — In a mountainous district, 150 miles north of Batopilas, November, *Palmer*, 376. Besides the entire leaves, the much shorter and firmer pappus-crown distinguishes this from the Arizonian *S. Plummeræ*.

**STEVIA MADRENSIS.** Subpedalis, scabrido-puberula vel glabella; ramis floridis subviscosis; foliis omnibus oppositis lanceolatis sessilibus membranaceis subtriplinerviis nervoso-venosis aut denticulatis aut fere integerrimis; capitulis laxè cymoso-fasciculatis subsessilibus; involucri bracteis (lin. 3 longis) obtusis; floribus lilacini-purpureis; acheniis glabellis; pappo coroniformi-concreto brevissimo. — Among Pines in ravines on the summit of the mountains, at about 8,800 feet, 150 miles north of Batopilas, October, *Palmer*, 328.

**STEVIA PALMERI.** Bipetalis, undique etiam ad involucria pilis brevibus patentibus mollibus pluriseptatis haud glandulosis subcanescens; foliis oppositis membranaceis subsessilibus obtusis, inferioribus oblongo-spathulatis bipollicaribus parum triplinerviis obtuse serratis basi cuneata integerrima, superioribus lanceolatis; cymis floribundis compositis; capitulis brevi-pedicellatis; involucri lin. 2 longi bracteis membranaceis acutiusculis; corolla alba, tubo brevi cum fauce lata extus villosa; acheniis glabris; pappo tripaleaceo et biaristato. — On the mountain-sides about 25 miles south of Batopilas, near the hacienda San Jose, *Palmer*, 30. Certainly allied to *S. paniculata*, Lag., possibly a very pubescent form of it.

**STEVIA LINOIDES**, Schultz Bip. in *Linnæa*, xxv. 284: var. *GRISEA*. Usque ad capitula crebra foliosissima, pube brevi canescens; corollis "flavido-albis." — In the mountains above Batopilas, at about 7,300 feet of elevation, October, *Palmer*, 251.

**STEVIA LAXIFLORA**, DC. Hort. Monsp., &c. *S. viscida*, HBK. Pine forest in the mountains, 150 miles north of Batopilas, *Palmer*, 418. To this must belong *S. amabilis*, Lemmon, first described in *Proc. Am. Acad.* xix. 1, where the character of the pappus is ambigu-

ously drawn by me. Note that it is the *paleæ*, and not the *aristæ*, which are extremely short.

CARPHOCHÆTE WISLIZENI, Gray, Pl. Fendl. 65, & Pl. Wright. i. 89. An interesting rediscovery of the original species of this genus, not very far from the original habitat, viz. on the Cumbre, or highest part of the mountains, above Batopilas, at about 8,000 feet, *Palmer*, 331.

PIPTOTHRIX, Nov. Gen. *Eupatoriacearum Ageratearum*.

Capitula pluriflora. Involucrum campanulatum, e bracteis 7-8 lanceolatis haud nervatis subæqualibus, 1-2 extimis parvis additis. Receptaculum nudum planum. Corolla fauce e tubo æquilongo angusto subito ampliata lato-campanulata, lobis brevibus ovatis patentibus. Antheræ appendice hyalina ovata obtusa terminatæ. Styli rami prælongi, filiformes, sursum parum incrassati, obtusi. Achenia pentagona *Eupatorii*. Pappus pauci-setosus, caducus, setis 6-12 tenuibus rigidis inæqualibus barbellato-scabris corolla brevioribus.

PIPTOTHRIX PALMERI. Suffrutex glabellus; ramis gracilibus patentissimis; foliis oppositis submembranaceis brevi-petiolatis ovato-lanceolatis plerumque acuminatis subserratis supra basim triplinerviis laxè venosis, venulis creberrime minuteque reticulatis; capitulis parvulis in cyma terminali aut corymbiformi aut paniculata; acheniis ad angulos parce hirtellis. — Forma  $\alpha$ , foliis bipollicaribus et ultra, floribus "albis." Under trees near springs in the mountains above Batopilas, at the Frailes, at about 7,000 feet, *Palmer*, 274. — Forma  $\beta$ , foliis minoribus nunc latoribus magis serratis, floribus ochroleucis. Forming underbrush, about four feet high, on the hillsides, apparently near the same station (*Palmer*, 280); the "bloom yellow" according to the collector's notes, but evidently no more than ochroleucous.

EUPATORIUM PALMERI. Bipedale, puberulum; caule suffrutescente ramisque gracilibus foliosis; foliis membranaceis oppositis ovatis et ovato-lanceolatis acuminatis (2-3-pollicaribus, petiolo  $\frac{1}{3}$ - $\frac{1}{2}$ -pollicari) basi quandoque subcordatis triplinerviis laxè venosis subserratis, pagina superiore glabella, inferiore pilis crispatis saltem ad venas tenui-pubescentibus; panicula terminali laxa inferne foliata; capitulis 8-10-floris lin. 2 longis; involucri bracteis 5-6 lanceolatis subtrinerviis æqualibus, 1-2 brevioribus additis; styli ramis apice breviter clavatis per anthesin breviter demum longiuscule exsertis; acheniis pubescentibus. — Shady places, high up in the mountains above Batopilas, *Palmer*, 144, 263. Somewhat related to *E. solidaginifolium*, Gray, but nearer

to *E. filicaule*, Schultz Bip. in herbariis, — of which, not being in Hemsley's work, probably no character has yet been published.\*

**EUPATORIUM STRICTUM.** Caulibus (ramisve) simplicissimis 2-3-pedalibus herbaceis minute puberulis cyma corymbosa polycephala terminatis; foliis oppositis dissitis (internodio dimidio brevioribus) orbiculatis subcordatis crenulatis serrulatisve (pollicaribus cum petiolo lin. 2 longo) submembranaceis hirsutulo-puberulis juxta basim trinervatis et divaricato-venosis, venis subtus prominentibus grosse reticulatis; capitulis lin. 3 longis pedicellatis; involucri campanulato 24-floro floribus paullo brevioribus, bracteis circ. 12 linearibus obtusiusculis æqualibus cum 1-2 brevioribus additis; corollis albis glabris; pappo albo; acheniis ad angulos hirtellis. — Sides of ravines under pine trees, near the Cumbre, or mountain summit above Batopilas, fully 8,000 feet of elevation, October, *Palmer*, 330.

**EUPATORIUM GRANDIDENTATUM**, DC. Prodr. v. 167, and probably *E. Pazcuarensis*, HBK., a narrow-leaved form. — Among rocks and bushes, 150 miles north of Batopilas, *Palmer*, 375.

**EUPATORIUM VENULOSUM.** *E. ageratoides* et *E. aromatici* soror, pariter ut videtur herbaceum, puberulum; foliis rhombeo-ovatis vel ovato-lanceolatis acuminatis (sesqui-bipollicaribus cum petiolo subsemipollicari) basi cuneata aut vix rotundata excepta argute modice-

\* *E. FILICAULE*, Schultz Bip. in herb. Berol., Gray, &c. Caule (herbaceo?) cum ramis gracillimis patentissimis tenui-puberulis; foliis fere glabris membranaceis oppositis longe petiolatis deltoideis ovatisque acuminatis obtuse dentatis vel denticulatis, basi truncata vel subcordata rariusve subhastata; capitulis secus ramos divergentes subaphyllos thyrsoides-racemosos; involucri 10-flori bracteis paucis lineari-lanceolatis. — Mexico, coll. *Ehrenberg*, no. 1176, and *Orizaba*, *Schaffner*, fide Schultz. We have it from *Orizaba*, coll. *Bilimek*, 1867, no. 576, and *Cordoba*, coll. *Bourgeau*, no. 1703. It needs to be compared with *E. polyotryum*, DC.

The following species is taken up from Seemann's collection:—

**EUPATORIUM MICROCEPHALUM.** Herbaceum (a basi?), vix puberulum; caule ultra-bipedali gracili subæqualiter folioso; foliis omnibus alternis ovatis acutis crenulato-serratis subtriplinerviis laxè venosis basi obtusa vel rotundata brevipetiolatis; panicula composita laxa ferrugineo-puberula; involucri simplici 5-6-phylo 5-6-floro lineam longo, bracteis lineari-oblongis corollisque extus resinoso-atomiferis; acheniis ad angulos parce hirtellis. — "N. W. Mexico," *Seemann*. Evidently the plant taken up by Hemsley, "Cerro de Pinal," as *E. incomptum*, DC.; but it is not at all the plant of *Bourgeau* (no. 3330), nor of *Liebmann*, so referred, the heads and flowers of which are very much larger, and in agreement with *DeCandolle's* character.

**EUPATORIUM AREOLARE**, DC., and *E. brevisetum*, DC., species placed next each other in the *Prodromus*, would appear to be one and the same. *Giesbreght's* no. 530 has the short pappus.

que serratis trinervatis, venulis subprominulis subtiliter reticulatis; cyma polycephala corymbosa; pedicellis gracilibus breviusculis; capitulis 8-10-floris (lin. 4 longis); involucri bracteis 8-10 oblongo-linearibus tenuibus extus glanduloso-pubentibus corollis albis nunc purpureo tinctis omnino glabris dimidio brevioribus. — Shady ravines under pine trees on the higher mountains (8,000 feet) above Batopilas, October, *Palmer*, 329. I do not identify this with any described species. The reticulation of the veinlets is more conspicuous and finer than in any of its allies.\*

**BRICKELLIA GLUTINOSA.** Frutex humilis, ramosissimus; foliis parvis (lin. 2-3 longis) cuneatis vel flabelliformibus inciso-dentatis coriaceis fere eveniis glutinosis in petiolum lamina parum breviorem attenuatis oppositis et alternis; capitulis brevi-pedunculatis ramulos terminantibus semipollicaribus circiter 15-floris; involucri bracteis obtusis, extimis lato-ovalibus, intimis linearibus; acheniis parce minuteque hispidulis. — S. W. Coahuila, on arid limestone cliffs of the mountains near Jimulco, Coahuila, *Pringle*, 143.

**BRICKELLIA BRACHIATA.** Inter *B. grandifloram* var. *minorem* et *B. Coulteri* collocanda, minute pubescens; caule erecto a basi ut videtur herbaceo bipedali ad apicem usque subæqualiter folioso; foliis (poll. 1-2 longis cum petiolo semipollicari) deltoideis vel hastato-subcordatis parce grosseque dentatis; capitulis sat numerosis longiuscule pedunculatis sparsisque in ramis divaricatis paniculæ cymæformis foliatæ; involucrio glabro cum floribus 10-12 semipollicari, bracteis fere omnibus obtusis, extimis ovalibus. — At the base of the mountains near Batopilas, in shade, *Palmer*, 169.†

**APLOPAPPUS TENULOBUS.** *A. aureo* affinis, subpedalis e radice annua, caule a basi ramoso cum involucrio viscoso-puberulo; foliis glabris in lobos angusto-lineares rhachi haud latiores setuloso-mucronatos pinnatipartitis; involucrio hemisphærico (lin. 5 alto), bracteis numerosis lineari-lanceolatis fere omnino herbaceis parum imbricatis discum æquantibus, exterioribus vix brevioribus; ligulis 15-20 ob-

\* Dr. Palmer also collected *Eupatorium collinum*, DC. (271), *E. Schaffneri* Schultz Bip. (332), *E. Guadalupe*, Spreng. (276), and *E. occidentale*, Hook., var. *arizonicum*, Gray, running into forms which will provoke the separation of this from the plant of the Pacific coast. Mr. Pringle collected the same plant (his 613), also *E. Greggii*, Gray (247), *E. Parryi*, Gray (135), *E. Wrightii*, Gray, (600), and *E. petiolare*, Moçino (266).

† *Brickellia simplex*, Gray, was collected both by Palmer (436) and by Pringle (641); the former obtained also some forms of *B. betonicaefolia*, Gray (434, 435), and the latter, forms of *B. Wislizeni*, Gray (323, 609), and several other species, also *Barroeta subuligera*, Gray (346).

longis (lin. 4 longis) læte aureis; styli ramis brevibus appendice ovato-lanceolata parte stigmatosa æquilongia; acheniis turbinatis villosissimis; pappo rigido valde inæquali, setis validioribus aristisve corolla disci brevioribus achenio duplo tantum longioribus. — Mountainous country about 150 miles north of Batopilas, *Palmer*, 408.

**ACHÆTOGERON PALMERI.** Glabellus, pube minuta strigulosa tantum puberulus; caulibus strictis bipedalibus e radice (ut in affinibus) perenni subæqualiter foliosis oligocephalis; foliis linearibus imisve subspathulatis integerrimis; involucri multibracteato striguloso-puberulis; ligulis perplurimis angustis albis (in tubulo pl. m. styliferis sed sterilibus?); styli ramis fl. herm. appendice brevi ovata obtusa superatis; ovariis obovatis compressis ad margines nervatis; pappo brevissimo setuloso-coroniformi. — Shady woods on the summit of the mountains above Batopilas, at about 8,800 feet, *Palmer*, 362.\*

**ACHÆTOTERON AFFINIS.** Præcedenti proximus, pilis patentibus (parte inferiore præsertim) hirsuto-pubescentibus; foliis membranaceis, inferioribus angusto-spathulatis acutatis rariter argute dentatis, summis linearibus integerrimis; capitulis dimidio minoribus; ligulis minus numerosis (40–50) albis ut videtur omnino *neutris*; styli ramis fl. herm. deltoideis acutissimis; acheniis parce puberulis subcompressis margine utroque tantum leviter uninervio; pappo brevissimo setuloso-coroniformi. — At the Frailles, about mid-height of the mountains above Batopilas, in shade under trees, *Palmer*, 255. The genus *Achætogeteron* is asserting itself as a necessity. The neutral rays of this species seem to be approximated by the preceding.

**ACHÆTOGERON PINNATIFIDUS.** Multicaulis e radice perenni, ultra-pedalis, pilis patentissimis undique hirsutus; foliis pinnatipartitis, segmentis linearibus rhachi æquilatis nunc latioribus sæpius integerrimis; involucri cinereo-hirsuto; ligulis perplurimis angustissime linearibus albis; acheniis compressis ovali-oblongis glabellis marginato-binervatis; pappo conspicuo coroniformi pluri-laciniato tertie parti longitudinis achenii adæquante. — On cool mountains west of Chihuahua, October, *Pringle*, 103. This is a true congener of *Achætogeteron Wislizeni*, Gray, which came from the same district in the mountains farther west, and has entire leaves. But it is so very like *Erigeron (Phalacrologma) Neo-Mexicanus*, Gray, in aspect, although specifically different, as to suggest the union of these four species of

\* *Psilactis asteroides*, Gray, Pl. Fendl., was collected by Palmer (410) north of Batopilas, therefore not very far from the station where Wislizenus found it, but in a more glandular and viscous form. *P. brevilingulata*, Schultz Bip., comes in Pringle's collection (14).

*Achæotogeron* with the *Phalacrolooma* or *Polyactidium* section of *Eriogeron*. Yet it would be very inconvenient to include in the latter genus species which have no pappus-bristles. On the other hand, the ambiguous *A. Seemanni* seems to have rudimentary bristles.

**ERIGERON (CÆNOTUS) INOPTATUS.** Hirsutus: caule valido ultrabipedali e basi ignota fastigiato- seu corymboso-ramosissimo; foliis laciniato-pinnatifidis vel parce inciso-dentatis, ramealibus sæpius integerrimis angusto-lanceolatis; capitulis subcymosis pedunculatis; involucri bracteis 2-3-seriatis subæquilongis lineari-lanceolatis acuminatis appressis, intimis scariosis; disco permultifloro cum receptaculo valde convexo; floribus fœmineis uniseriatis, ligula oblonga vel lineari stylum suum parum et flores hermaphroditos haud superante; achenis glabris; pappo e setis paucis corolla brevioribus albis barbellulatis caducis. — On river-bank in sand, 150 miles north of Batopilas, *Palmer*, 442. A coarse plant, of anomalous habit and character. Heads a quarter of an inch in diameter.

**GNAPHALIUM PRINGLEI.** Annuum vel bienne, sesquipedale; foliis radicalibus spathulatis, caulinis lanceolatis acutiusculis (summis vix apiculatis) basi breviter adnato-decurrentibus subtus tenui-lanatis supra cum caule ramisque pube brevissima viscidula indutis; capitulis parvulis (lin. 2 longis) glomerato-cymosis; involuero cylindraceo, bracteis albidis obtusiusculis, extimis angusto-oblongis, intimis linearibus. — Near Chihuahua, under cliffs, Oct., *Pringle*, 305.

**LAGASCEA DECIPIENS**, Hemsl. Biol. Centr.-Am. Bot. ii. 140, t. 44. San Miguel, near Batopilas, on the mountain-sides, *Palmer*, 145. "Compact shrubby plants, with abundance of golden-yellow blooms." The deep yellow color of the corollas is well preserved in the excellent dried specimens. The flowers of Seemann's plant were probably of the same color, but the specimens do not show it. In both, the upper part of the akene, as well as the pappus, is more or less villous.

**GUARDIOLA TULOCARPUS**, Gray, var. **ARGUTA.** Elatior e caudice perenni; foliis plerisque lanceolatis inæqualiter argute dentatis, quandoque modo *G. atriplicifoliæ* dente infimo utrinque protracto subhastatis; involuero lin. 4-5 longo, fructifero ovoideo-fusiformi; floribus fœmineis achenisque nunc 2. — Rocky hills west of the city of Chihuahua, "growing in large clumps," *Pringle*, 678. The root is evidently perennial; but the foliage is too like that of *G. atriplicifolia*. — The North American *G. platyphylla*, Gray, was brought by *Palmer* (35) from the mountains south of Batopilas.

**MELAMPODIUM LONGICORNU**, Gray. The enclosing fructiferous bracts become strongly tuberculate in *Pringle's* Chihuahua specimens,

in those of Palmer (245), and hardly less so in those of Lemmon from S. Arizona. They are described in Syn. Fl. i.<sup>2</sup> 239 as "little tuberculate or smooth."

**PARTHENIUM TOMENTOSUM**, DC. Prodr. v. 332. River-bank, near Batopilas, *Palmer*, 123. "A large, bushy plant, 5 feet high," with leaves 7 or 8 inches long and a petiole of 2 inches. No pappus. Appears to agree well with DeCandolle's species, which comes, however, from the southern State of Oaxaca.

**TRAGOCEROS MOCINIANUS**. *T. zinnoides*, HBK., perquam similis; ligulis apice tantum bifidis haud fissilibus; costis achenii tuberculatis. — *Zinnia bicuspis*, DC. Prodr. v. 535, Mocino & Sessé, Ic. Fl. Mex. t. 573, in which the rude figure from which DeCandolle took the character "achæniis disci uniaristatis" was probably misapprehended. Benthams may with reason suspect that the described species should be reduced; and DeCandolle's two sections are probably of no account; for the tuberculation of the akenes does not appear on the well-grown ovary of the present plant, and in other genera this is a fallacious character. But inasmuch as this plant has not the divided and two-horned ligules of the original species, and has strongly tuberculate ribs, it may for the present be kept distinct. The larger heads and the long rays distinguish it from *T. Schiedeianus*. — Hills at San Jose, south of Batopilas, with "creamy white bloom," *Palmer*, 67.

**ZALUZANIA DISCOIDEA**. *Z. angustæ* et *Z. mollissima* vere congener, sed herbacea e. rhizomatibus repentibus et ligulis nullis; pube minuta canescens; caule simplici 2-4-pedali e basi parum lignescente; foliis lato-ovatis brevi-petiolatis subintegerrimis amplis (sæpius 4-pollicaribus) supra glabratis viridulis subtus albo-tomentulosis; capitulis parvulis (lin. 3 altis) subglobosis plurimis in cymam nudam fastigiato-compositam digestis; involucri brevi adpresso canescente; corollis achenio brevioribus. — Along streams among the hills west of Chihuahua, *Pringle*, 309.

**MONTANOA PATENS**. Fruticosa, tenuiter puberula; caule orgyali laxè ramoso; ramis floridis gracilibus patentissimis capitula sparsim cymosa graciliter pedunculata gerentibus; foliis membranaceis acuminatis subserrulatis, caulinis (inferioribus haud visis) superioribus deltoideo-ovatis angulatim sub-3-5-lobatis juxta basim sæpe biauriculato-appendiculatam triplinerviis (poll. 4-5-longis et petiolo nudo sequipollicari), ramorum ovato-lanceolatis subintegris; involucri bracteis angustis disco lin. 2-3 alto paullo brevioribus; ligulis 6-8 obovatis lin. 4-5 longis albis; paleis receptaculi per anthesin ovato-oblongis mucrone mox recurvo apiculatis, fructiferis maxime ampliatis charta-

ceo-scariosis obovato-cuneatis cucullatis glabris achenio pyriformi involventibus. — Shady places in the mountains above Batopilas, *Palmer*, 164. Character wholly from Dr. Palmer's specimens, in flower, and also some in fruit. But the species may probably include the plant collected by Seemann in the Sierra Madre of Durango, referred by Schultz Bip., Bot. Herald, 304, to his *Montagnea atriplicifolia*. Our specimen of this is incomplete, and it has larger ligules. Schultz was probably right in identifying *Verbesina atriplicifolia*, Juss., DC., and Colla, Hort. Rip. 144, t. 31, with *M. arborescens*, DC., but surely he is not to be followed in the making of a new name for it on account of this identification. A comparison with Colla's description and figure of *M. arborescens* (under the above-mentioned name) makes it clear that to this may be referred the *M. grandiflora*, Benth. Pl. Hartw. no. 134 (not of DC.), a species which comes nearest to *M. frutescens*.\*

**HELIANTHELLA PRINGLEI.** Species singularis, hispidulo-scabrella; caulibus e caudice lignescente pluribus ultra-pedalibus ad apicem usque æqualiter foliosis; foliis ellipticis (circ. bipollicaribus siccitate chartaceis nitidulis) uninerviis venulosis basi parum angustata sessilibus; capitulo sat pedunculato ultra-semipollicari; involuero fere glabro, bracteis subulato-linearibus laxis, iis receptaculi chartaceis obtusis; ligulis lin. 7-8 longis linearibus; acheniis immaturis lineari-oblongis (extimis nunc 3-4-gonis) cano-villosis breviter biaristatis; squamellis intermediis aut nullis aut inter pilos achenii evanidis. — On rocky hills west of Chihuahua, Sept., *Pringle*, 646.

**VERBESINA CHIHUAHUENSIS.** *V. Wrightii*, Gray soror, gracilior, magis ramosa; foliis plerisque in petiolum attenuatis, aut omnibus lanceolatis dentato-incisis rariusve subintegerrimis alternis, aut inferioribus oppositis latioribus basi abruptis; capitulis parvulis (lin. 4 altis); involuero brevi laxiore; acheniis hirsutulis plerumque longiuscule biaristatis. — Santa Eulalia Mountains, near Chihuahua, on limestone, in cañons, *Pringle*, 657.

**VERBESINA LEPTOCHÆTA.** Inter *Pterophyta aptera*, *V. Wrightii* parum similis, frutescens; foliis oppositis serratis hispidulo-scabris triplinerviis, caulinis deltoideis (4-5-pollicaribus), ramealibus ovato-lanceolatis, omnibus in petiolum alato-marginatum subito decurrentibus; capitulis subsolitariis pedunculatis majusculis (ultra-semipolli-

\* No. 535, Ghiesbreght, Chiapas, coll. 1864-70, referred to *M. arborescens* by Hemsley, probably through my wrong naming of a specimen sent from this herbarium to that of Kew, is a very different species; but before naming it one should compare the several species of Schultz published by Koch in *Wochenschr.* vii., here unknown.

caribus) multifloris; involucri laxi bracteis exterioribus herbaceis angusto-oblongis disco brevioribus patentissimis (demum deciduis), interioribus erectis membranaceis; floribus radii paucis styliiferis sed sterilibus, ligula parvula lineari; acheniis disci elongato-oblongis angusto-alatis nunc subulatis lin. 3-4 longis aristis pappi 2 gracilibus vix duplo longioribus. — Near Batopilas, *Palmer*, 170. "A bushy plant, sunflower-like, 5 to 8 feet high," the branches herbaceous, but at least frutescent below; stems not at all wing-margined.

**VERBESINA CYMOSA.** *Verbesinaria*, e grege *V. arborea*, fruticosa, ultra-orgyalis, tomentulosa; ramis foliosis exalatis cyma composita corymbiformi polycephala aperta terminatis; foliis oppositis lanceolatis utrinque attenuatis serrulatis penninerviis (6-9 poll. longis cum petiolo brevi) supra hispidulo-scabris subtus canescenti-sericeis; capitulis pedicellatis angusto-oblongis 7-9-floris; involuero duplici, nempe e bracteis 8-9 lanceolatis obtusiusculis viridulis erectis biseriatim imbricatis disco dimidio brevioribus et totidem tenuioribus lineari-oblongis flavescentibus flores subæquantibus paleis receptaculi referentibus; acheniis ignotis; ovario brevi obovato biaristato; aristis filiformibus sed obcompressis puberulis corolla paullo brevioribus. — Mountain ravines near Batopilas, "upright, many-stemmed, 8 feet high, with golden-yellow blossoms," *Palmer*, 135.

**BIDENS LUDENS.** *Psilocarpæa*, annua, glabra; caule bipedali ramoso corymboso-floribundo; foliis tenuibus bipinnatipartitis, lobis linearibus; involuero campanulato (lin. 2-3 alto), bracteis exterioribus patentibus linearibus vel lineari-spathulatis hirtello-ciliatis; ligulis (neutris) conspicuis ovalibus (lin. 3 longis) aureis; acheniis hirtello-scabris tetragonis heteromorphis, extimis obovato-clavatis sesquilinearibus calvis, interioribus sensim longioribus angustioribus, intimis (lin. 3 longis) fere linearibus basi apiceque parum attenuatis aut calvis aut breviter biaristatis, aristis subulatis versus apicem setis 2-4 validis retrorsis (persistentibus vel deciduis!) barbatis. — Cool hillsides and along streams, northwest of the city of Chihuahua, *Pringle*, 293, very sparingly collected.

**LEPTOSYNE (COREOCARPUS) ARIZONICA**, Gray, Proc. Am. Acad. xvii. 218, & Syn. Fl. i.<sup>2</sup> 301. Found on the mountains behind Batopilas, at about 7,000 feet, *Palmer*, 294.

**TRIDAX ERECTA.** Hispida vel hispidula; caule erecto paniculatim ramoso e radice annua (nec modo peraffinis *T. procumbentis* procumbente e radice perenni), ultrapedalis; foliis membranaceis aut ovalibus dentatis aut dilatatis trifidis, lobis denticulatis rariter incis; ligulis brevibus saturate luteis; paleis receptaculi costa excurrente aristatis;

pappo e setis 20 longe plumosis corolla disci dimidio achenio paullo brevioribus. — Among rocks midway on the mountains above Batopilas, *Palmer*, 285.

*TRIDAX BICOLOR*, Gray, Pl. Fendl. 104. Mountain-sides above Batopilas, *Palmer*, 130. Rays bright white (disk yellow): but specimens of Pringle (638), from near the city of Chihuahua, have the rays tinged with rose. Both are larger-leaved than the original specimen of coll. Wislizenus.

*TRIDAX LEPTOPHYLLA*. Parce hispidula; caule (e radice annua?) erecto patenti-ramoso pedali; ramis superne longe nudis monocephalis; foliis ternato-nunc biternato-partitis in segmenta angusto-linearia elongata integerrima, summis nunc integris fere filiformibus; capitulis multifloris; disco fructifero fere conico (semipollicari); involuero lato-campanulato, bracteis ovalibus vel orbiculatis membranaceis purpurascensibus glabris; paleis receptaculi demum alte conici muticis; ligulis rotundato-quadratis tubo suo villosa subduplo longioribus discique corollis aureis; pappi setis rigidis breviter plumosis achenio turbinato aequilongis. — Sandbars of the river near Batopilas, *Palmer*, 425.

*PERITYLE MICROCEPHALA*. Cinereo-puberula, e radice forte annua ramosissima, diffusa, floribunda; foliis omnibus oppositis deltoideis seu dilatato-ovatis basi truncatis grosse paucidentatis repandisve (lin. 4–8 longis); capitulis subcymosis (lin. 2 altis); involucri late campanulati bracteis oblongis; ligulis albis quadratis lineam longis; corollis disci brevibus; styli fl. herm. ramis cono subulato terminatis; acheniis oblongis marginibus dense villosis; pappo coroniformi sat conspicuo sæpius cum aristellis 1–2 tenuibus nudis achenio circiter dimidio brevioribus. — Rocky hills near the city of Chihuahua, Oct. 8, just coming into blossom, *Pringle*, 571 (too scanty for distribution\*), and mountains above Batopilas late in October, with mature akenes, *Palmer*, 268. The delicate awns of the pappus under the lens are either quite smooth or occasionally with one or two denticulations.

*BAHIA NEO-MEXICANA*, Gray, Proc. Am. Acad. xix. 27, & Syn. Fl. i.<sup>2</sup> 333. North of Batopilas, *Palmer*, 399; also coll. by *Pringle*.

*SCHKUHRIA WISLIZENI*, Gray, Pl. Fendl. 96. About 150 miles north of Batopilas (therefore not far from where it was discovered by Wislizenus), *Palmer*, 387. A larger and much-branched form.

*HYMENOTHRIX PALMERI*. Ultrapedalis e radice forte annua, subglabra; foliis ternatipartitis et segmentis subpinnatipartitis in lobos 3–7 angusto-lineares integerrimos, summis parvulis trifidis; inflores-

\* The rare *Perityle Parryi*, Gray, is, however, in *Pringle's* distribution, 183.

centia generis; capitulis hemisphaericis multifloris; involucri bracteis flavo tinctis; ligulis nullis; corollis flavis, lobis ovatis fauce lato-campanulata æquilongis; acheniis obpyramidatis acutissime 4-5-gonis, angulis villosissimis; pappo corolla et achenio brevior insigniter paleaceo, nempe e paleis 12 lato-lanceolatis oblongisve costa valida excurrente aristellatis vel fl. exteriorum quandoque muticis. — In the mountainous district 150 miles north of Batopilas, *Palmer*, 395. A very interesting species in that it seems to connect the rayless *H. Wrightii* with the radiate and yellow-flowered *H. Wislizeni*; but not so welcome in that the paleaceous and only awn-tipped rays of the pappus indicate an approach to *Bahia*. The corolla and involucre, however, are truly of *Hymenothrix*.

POROPHYLLUM SEEMANNI, Schultz Bip. in Seem. Bot. Herald, 308. Near Batopilas, *Palmer*, 216.

TAGETES WISLIZENI, Gray, Pl. Fendl. 92. *Leptocephala*, spithamæa ad pedalem e radice annua; ramis gracilibus patentibus uni-paucifloris; pedunculis capitulo parum longioribus; foliis pinnatisectis, segmentis 7-13 (haud ultra-semipollicaribus summis confluentibus) anguste-lanceolatis acutis inciso-dentatis, dentibus acutis muticis foliorum suprem. parvulorum tantum setiferis; involucri fusiformi semipollicari 4-5-dentato 8-12-floro; ligulis 2-4 rotundatis lineam longis; pappo e paleis 1-2 sensim subulato-aristatis achenio æquilongis totidemque truncatis dimidio brevioribus, omnibus sæpius tubuloso-concretis. — On the mountains at about 7,000 feet, half-way between Batopilas, and on the *Cumbre* or summit, *Palmer*, 267. The specimen of *Wislizenus* is depauperate. In Proc. Am. Acad. xix. 43, I have cited it under *T. subulata*, the *T. multiseta* of DeCandolle. But now the present good specimens show that the leaves are none of them bipinnately dissected, and only the bracteiform ones are setiferous.

TAGETES PALMERI. Perennis; caule quadripedali ramoso inferne frutescente; ramis ad apicem usque foliosis; foliis pinnatisectis, segmentis angustis lanceolatis sensim acuminatis acutissime serrulatis (poll. 1-2 longis, imis cum paucis hinc inde interjectis parvis subsetiferis); pedunculis corymboso-fastigiatis ultra-pollicaribus inferne gracilibus sursum crassioribus; involucri multifloro lato-campanulato (vix ultra lin. 3 alto) 8-10-dentato disco brevior; ligulis 5-8 obovato-oblongis emarginatis semipollicaribus croceis; pappo e paleis sæpius 2 subulatis aristiformibus cum 2-3 brevibus quadratis truncatis. — Same habitat as the preceding, "near a spring, very showy and many-flowered," *Palmer*, 267. To be associated with *T. Parryi* and *T. Lemmoni* rather than with *T. patula*.

PECTIS BERLANDIERI, DC.? var. PALMERI. Pedunculis sparsis longioribus quandoque pollicaribus; pappi setis 2-3. — South of Batopilas, *Palmer*, 61.

PECTIS STENOPHYLLA. *Pectothrix*, *P. longipedi* quoad flores per-similis, e basi suffrutescente ramosissima, diffusa, subpedalis; ramis gracillimis foliosis; foliis angustissime linearibus tenuibus; pedunculis capillaribus sesquipollicaribus; involuero (lin. 2 alto) angusto circa 8-phyllo 15-18-floro; ligulis 8. — Hillsides near Batopilas, *Palmer*, 81. Pappus of *P. longipes*, or the awns of the ray-flowers stouter.

ARTEMISIA REDOLENS. *Dracunculus*, e radice perenni ultrapedalis, quoad surculos radicales cano-tomentulosa, cæterum viridis glabella vel glabra; foliis tenuibus 3-5-partitis in segmenta linearia (vix ultra-semi-pollicaria) subintegra; capitulis sesquilineam longis paniculatis erectis; involuero glabro; acheniis pallidis opacis costato-striatis. — Chihuahua, on cool slopes under cliffs, *Pringle*, 296. Bears some resemblance to *A. dracunculoides*; "has a powerful odor like that of *A. Absinthium*, but stronger, which burdens the air of the whole hillside."

SENECIO HARTWEGI, Benth. Pl. Hartw. 18; Gray, Syn. Fl. i.<sup>2</sup> 386. Mountainous district, 150 miles north of Batopilas (therefore not far from where it was collected by Wislizenus), *Palmer*, 366.

PEREZIA PLATYPHYLLA, Gray, Pl. Fendl. 111, & Proc. Am. Acad. xix. 61. Santa Eulalia Mountains, Chihuahua, *Pringle*, 583. At Yerba Buena, Chihuahua, about 7,000 feet above the sea, *Palmer*, 299. The round leaves maintain the character of the species, as founded on the specimen gathered by Wislizenus in this region.

PEREZIA THURBERI, Gray, Mem. Am. Acad. v. 324, & Syn. Fl. i.<sup>2</sup> 409. Rocky hills near Batopilas, *Palmer*, 212.

PEREZIA PANICULATA. Scabrido-puberula; caule elato ramoso; foliis (inferioribus ignotis) chartaceo-membranaceis (3-4-pollicaribus) lanceolatis acutis deorsum angustatis basi acutis subsessilibus penninerviis venuloso-reticulatis subintegerrimis; panicula floribunda laxa; capitulis pro genere parvis; involuero campanulato (lin. 2-3 longo) 10-12-floro, bracteis 3-4-seriatim imbricatis coriaceis acutis vel apiculatis margine villosulis, versus apicem viridibus vel purpureo tinctis, extimis ovatis, intimis lineari-oblongis. — Mountains above Batopilas, at the Frailes, about 7,000 feet above sea level, *Palmer*, 279.

#### *Lobeliaceæ.*

LOBELIA GRACILENS. *L. gruinæ*, Cav. proxima; radicibus fasciculatis incrassatis; caulibus 1-2-pedalibus gracillimis; foliis radicalibus rosulatis angusto-spathulatis (pollicaribus), caulinis linearibus angustis-

simis integerrimis, summis filiformibus; floribus paucis in racemo laxo longe pedicellatis; corolla cærulea majuscula, lobis labii majoris semipollicaribus oblongis tubo parum longioribus. — Grassy places, on the summit of the mountains above Batopilas, at about 8,850 feet, *Palmer*, 360. No. 29 of Coulter's Mexican collection is probably a larger-leaved form of this species, but my specimen is insufficient.

*Apocynaceæ.*

PLUMERIA MEXICANA, Lodd. Bot. Cab. t. 1024? *P. Lambertiana*, Lindl. Bot. Reg. t. 1378? *P. mollis*, Benth. Pl. Hartw. 24, non HBK. — "Trunk erect, 10 or 15 feet high, 6 inches in diameter, with few short and stiff branches." Rocky hillsides, near Batopilas, *Palmer*, 231. This cannot be *P. mollis*, HBK., from the Orinoco, which is said to have a repent or prostrate trunk, and the leaves pubescent beneath. Hartweg's specimens are in blossom, *Palmer*'s in fruit, with follicles terete and slender, half a foot long. Body of the seed half an inch long, thin, extended downwardly (toward base of follicle) into thin wing of nearly an inch in length. With our present knowledge it is better to take these names as of one species, and to adopt the oldest name.

TABERNÆMONTANA ———. Allied to *T. littoralis*, HBK., or at least to no. 2222 of Bourgeau's coll. at Cordoba, but thinner-leaved. In fruit only. Follicles globose-ovate, inch and a half long, with evidently fleshy epicarp, dehiscent, very many-seeded. Seeds enclosed in a scarlet arilliform pulp, the firm and elongated-oblong body 4 lines long, lightly striate; albumen ruminant at the surface. — In ravines near Batopilas: "a large loose-growing shrub, with dark green foliage, said to be poisonous," *Palmer*, *M.*

TRACHELOSPERMUM STANS. Fruticulus erectus, bi-tripedalis; foliis fere *T. difformis*; pedunculis brevioribus; floribus haud visis. — Near the city of Chihuahua, under cliffs, *Pringle*, 640. One would expect the *T. difforme* collected at Monterey to be the same, but that is twining, and seems to be the United States species.

*Asclepiadaceæ.*

PHILIBERTIA PALMERI. Inter *P. elegantem* et *P. viminalem* quasi media, tenuiter puberula, volubilis; foliis (plerumque pollicaribus) oblongis apiculato-acuminatis basi rotundatis vel obtusis brevipetiolatis; pedunculis foliis umbellaque multiflora ter longioribus; corollæ albæ suaveolentis lobis obtusissimis lin. 3 longis; corona exteriore annulato conspicuo, interiore peraffinium. — Banks of

streams near Batopilas, climbing over bushes, *Palmer*, 5. Has the long peduncles and nearly the foliage of *P. viminalis*, but a minute pubescence, and the exterior crown much more manifest. The gravid ovary is ovate and densely canescent-tomentose. But a follicle accompanying our specimen is slender-fusiform and glabrous.

*PHILIBERTIA ELEGANS*, Gray, Syn. Fl. ii.<sup>1</sup> 87, under *P. Torreya*. The latter species is distinguished from the former, not so much by the characters assigned in the work cited as by the very much thickened pieces of the inner corona. The specimens of *P. elegans* collected by *Pringle* in Chihuahua are very pubescent, and the umbels many-flowered. The divisions or scales of the inner crown in this species, when fresh or freshened by soaking, are seen to be "rotund," as described by *Decaisne*, pointless, and decidedly flat. The peduncles vary in length, are sometimes short, but never much longer than the pedicels. *P. bicolor* (*Sarcostemma bicolor*, *Decaisne*), which *Hemsley* unites with *P. elegans*, may be a variety of it; but it has, as described, sessile umbels and scales of the inner corona ovate with an acumination. With this agrees *Bourgeau's* no. 318 from Santa Fé in the valley of Mexico, except that these scales are only mucronate-apiculate; also *Schaffner's* no. 640, in which they are less apiculate.

*PHILIBERTIA BILOBA*, the *Sarcostemma bilobum*, *Hook. & Arn.* Bot. Beech. 438, has probably been wrongly suppressed in *Hemsley*, Biol. Centr.-Am. Bot. ii. 318, although he should have had the original at hand. It comes from Acapulco only, and is said to have the divisions of the staminal crown ovato-triangular. Those of *P. cynanchoides* (of widely different habitat) are broadly oval, very obtuse and turgid. The following, from the eastern side of Mexico, may be more like *P. biloba*.

*PHILIBERTIA ERVENDBERGII*. Volubilis, undique puberula; foliis ovato-cordatis (sinu aperto lobis rotundatis) tenuiter acuminulatis parum sesquipollicaribus; umbellis pedunculatis; corollæ glabellæ lobis ovato-ellipticis obtusis (lin. 3-4 longis) viridulis intus linea purpurea notatis mox reflexis; corona exteriore annulari conspicua gynostegium fere lineam longum æquante, interiore e squamis crassiusculis verticalibus latissime oblique ovatis apice libero acutiusculis antheris parum brevioribus. — *Sarcostemma elegans*, Gray, Proc. Am. Acad. v. 187. — *Wartenberg*, near Tantoyuca, Mexico, *Ervendberg*, coll. no. 174. The following species also appears to be new:—

*PHILIBERTIA FENDLERI*. Volubilis, fere glabra; foliis sinu angusto profundo cordatis ovatis subito acuminatis (2-3-pollicaribus); pedunculo pedicellisque umbellæ multifloræ elongatis; corollæ fere

glabræ lobis oblongis (lin. 4 longis) pallidis mox reflexis; corona exteriore annulari margine tenui integerrimo gynostegium fere lineam longum æquante, interiore e squamis crassis rotundo-ovalibus antheris parallelis basi earum adnatis discum stigmatis paullulum superantibus. — Tovar, Venezuela, *Fendler*, coll. no. 2119.

**METASTELMA PRINGLEI**, n. sp. Rocky hills around Chihuahua, *Pringle*, 62. Species nearest *M. Chiapense*. — In the subjoined footnote I have attempted to characterize the known species of Mexico and the United States.\*

\* **METASTELMA**, R. Br. Species Am. Bor. et Mex.

Schlechtendal's *Irmishia* (*floribunda*), with its large leaves, compound cymes, and structure of flower not wholly clear, is probably not of this genus, and so ought not to give the name of Bentham and Hooker's first section. Nor are their three sections very definitely marked. *M. pedunculare*, Decaisne, attributed to Mexico by him, was of the Guatemalan part of Hartweg's collection. In all the following species known to us, (except perhaps the first, which is variable,) the peduncles are short, often very short or nearly wanting.

\* Columna (i. e. tubus stamineus) elongata, coronam sub antheris gerens: corolla campanulata 5-fida. — § *Epicion*, Griseb.

**M. BAHAMENSE**, Griseb. Cat. Cub. 174; Gray, Syn. Fl. ii. 101. — Florida. (Bahamas.)

\*\* Columna manifesta sed brevis, coronam juxta antheras gerens: corolla 5-partita, imberbis, lineam longa.

**M. SCHAFFNERI**. Glabrum, tenue; foliis lanceolatis basi obtusis; calycis lobis subulatis; corollæ subquinquepartitæ lobis oblongo-ovatis crassiusculis intus tantum puberulis; columna antheris subæquilonga; coronæ squamis lineari-subulatis discum stigmatis superantibus. — *Metastelma Palmeri*, Watson, Proc. Am. Acad. xviii. 115, quoad pl. Schaffner. — Mexico, near San Luis Potosi, *Schaffner*, part of no. 652, misprinted 635 in Proc. Am. Acad. l. c.

**M. ANGUSTIFOLIUM**, Turcz. Præter caules striolatos lineato-puberulos pedilosque glabrum; foliis lineari-lanceolatis basi acutis; calycis lobis ovatis; corollæ profunde quinquepartitæ prorsus glabræ lobis ovatis; columna brevissima; coronæ squamis lato-ovatis subito acuminatis membranaceis contiguis antheras æquantibus. — Bull. Soc. Nat. Mosc., 1852, ii. 15, & Flora, 1853, 721, ex char. *M. Palmeri*, Watson, l. c., as to pl. Bourgeau. — Mexico, *Linden*, no. 1353. *Bourgeau*, no. 627.

\*\*\* Columna nulla vel brevis: corona ad juncturam andræcii et corollæ 5-partitæ inserta.

← Corolla haud ultra sesquilineam longa, intus glabella, minute cano-papillosa vel puberula, nunquam villosa-pubescent: herbæ glabræ.

↔ *Angustifolia*.

**M. PALMERI**, Watson, pro parte. Foliis angusto-lanceolatis basi acutiusculis vel obtusis: calycis lobis ovatis obtusis; corollæ lobis oblongis seu oblongo-lanceolatis; coronæ squamis lanceolatis acuminatis vel ovato-subulatis discum

**GONOLOBUS PETIOLARIS.** Subvolubilis, e basi frutescente 2-3-pedalis, parce hirsutus; foliis tantum pubescentibus membranaceis oblongo-cordatis acuminatis sesqui-tripollicaribus et petiolo æquilongi; pedunculis petiolo haud longioribus laxè plurifloris; sepalis lanceolatis (lin. 2 longis); corolla aut fusco-purpurascens aut "alba" rotata 5-partita glabra lævique haud incrassata, lobis lanceolatis (adultis vix semipollicaribus); corona simplici subcarnosa crateriformi vix quinqueloba truncata; folliculi desunt. — Margins of ravines, &c., near Batopilas, *Palmer*, 7, 208.

planum stigmatis paullo superantibus. — Gray, Syn. Fl. ii. 403. *M. Palmeri* (quoad pl. *Palmer*, no. 824) & *M. Californicum* (pl. *Palmer*, 828), *Watson*, Proc. Am. Acad. xviii. 115. — Southern borders of Texas, at Laredo, *Palmer*, and farther westward in Kimble Co., *Reverchon*. Also, adjacent Mexico, in mountains south of Monclova, *Palmer*.

↔ ↔ Latifolia.

**M. CALIFORNICUM**, Benth. Bot. Sulph. 33, t. 18. — Bay of Magdalena, Lower California, *Hinds*. Not since collected; said to be similar to the next, the ovate-oblong leaves commonly subcordate, the corolla in bud globular and its lobes broadly ovate; and the lanceolate scales of the corona little surpassing the stigma.

**M. PARVIFLORUM**, R. Br., of the West Indies, has been cited from Mexico: if so, it must belong to the coast districts. *M. Fraseri*, Decaisne in DC. Prodr. viii. 513, may belong here. It was described from a specimen in Bentham's herbarium, received from that of Forsyth, and thought perhaps to come from Carolina, but most probably from the West Indies.

← ← Corolla lin. 1-2 longa, lobis intus pubescentibus vel villosis: folia lanceolata et linearia.

**M. CHIAPENSE.** Vix volubile, fere glabrum; foliis linearibus acuminatis vel acutatis (lin. 6-12 longis 1-1½ latis) basi subacutis, superioribus cymulas subsessiles 3-6-floras paullo superantibus: calycis lobis ovatis obtusis: corolla in alabastro ovoidea (lineam longa), lobis ovatis acutiusculis crassiusculis intus crebre breviter pubescentibus; columna vix ulla; coronæ squamis angustissime linearibus corollæ lobis tertia parte brevioribus vertice stigmatis pyramidato emarginato adæquantibus. — *M. Cubense*? Hemsl. Biol. Centr.-Am. Bot. ii. 327, non Decaisne. *M. Palmeri*, *Watson*, l. c., quoad pl. *Ghiesbreght*. — On arid mountains, in Chiapas, S. Mexico, *Ghiesbreght*, no. 664.

**M. PRINGLEI.** Vix volubile, humile, glabrum; foliis lanceolatis nunc lineari-oblongis acutis vel obtusis mucronatis (lin. 6-12 longis 2-3 latis) basi rotundatis vel retusis cymulas subsessiles 2-5-floras superantibus; calycis lobis oblongis obtusis; corolla in alabastro oblongo-ovoidea (sesquilineam longa), lobis angustoblongis intus retrorsum denseque villosopubescentibus; columna brevissima; coronæ squamis fere filiformibus acutatis corollæ lobis paullo brevioribus discum convexum stigmatis longius superantibus. — Chihuahua, N. Mexico, *Pringle*, no. 62. Vide supra.

**M. ARIZONICUM**, Gray. Volubile, puberulum, basi lignescens; ramis rigi-

**GONOLOBUS STENOPETALUS.** *G. obliquo* peraffinis, multo humilior, pedalis ad orgyalem e basi lignosa, primum erecta, parum volubilis, hispidior; foliis profunde cordatis subito-acuminatis 2-4-pollicaribus et petiolo fere æquilongo; cymis plurifloris cum pedunculo brevi petiolo brevioribus; calyce hispidulo; corolla glabra vel extus glabriuscula virido-purpurea 5-partita, segmentis lineari-ligulatis ( $\frac{3}{4}$ -1-pollicaribus); corona antheris brevior atropurpurea annuliformi carnosa 5-lobata, lobis crassis (apice brevi inflexis) subglobosis; folliculis turgido-ovatis brevi-acuminatis hirsutulis muriculatis; seminibus haud comosis! — Shaded and rocky hills near Chihuahua, *Pringle*, 55, 696.

**GONOLOBUS CHIHUAHUENSIS.** Facies omnino *Chthamaliæ*, corona simplici *Eugonolobi*, procumbenti-diffusus, nec volubilis, undique hirsutus; caulibus subpedalibus foliosissimis; foliis ovatis subcordatis acutis (haud ultrapollicaribus) petiolatis margine sæpius undulato-crispis; pedunculo 1-3-floro folium æquante; corolla (purpurascente) glabra 5-partita, lobis oblongis lin. 2 longis tenuiter nervosis et versus apicem reticulatis; corona brevi patelliformi margine lobis 5 angustissime linearibus puberulis antheris crassiusculis oppositis super eumque incumbentibus instructis; folliculis turgido-ovatis acuminatis hirsutulis muricatis. — On hills and mesas around the city of Chihuahua, *Prin-*

dulis; foliis crassiusculis nunc angusto- nunc oblongo-linearibus; floribus ob pedunculum pedicellosque brevissimos in axillis glomeratis; calycis lobis subulatis rigidulis corolla dimidio brevioribus; corollæ profunde 5-partite lobis crassiusculis lineari-lanceolatis intus creberrime villosopubescentibus; coronæ squamis lineari-subulatis discum umbonatum stigmatis paullo superantibus. — Proc. Am. Acad. xix. 85, & Syn. Fl. ii. 403. — S. Arizona, near Tucson, *Pringle*.

**M. BLODGETTII**, Gray. Volubilis, glabrum; caulibus filiformibus; foliis tenuioribus angustissime lanceolatis; floribus pedicellatis in cymula 1-5-flora laxa brevipedunculata; calycis lobis ovatis brevibus; corollæ lobis lineari-lanceolatis intus basi nudis supra medium hirsutulo-barbatis; coronæ squamis lineari-subulatis discum stigmatis æquantibus. — Proc. Am. Acad. xii. 73, & Syn. Fl. ii. 101. *M. parviflorum*, Chapm. Fl. 367, non R. Br.

— + + Corolla lin. 2-3 longa, profunde 5-partita, lobis linearibus intus creberrime villosopubescentibus: folia ovato-oblonga seu lanceolata coronæ squamæ attenuato-subulate.

**M. BARBIGERUM**, Scheele in Linnæa, xxi. 760, &c. — Texas; first coll. by *Berlandier*.

\* \* \* \* Columna antheris æquilonga, nuda: corona (e squamis angustissime linearibus) basi corollæ fere 5-partitæ inserta: folia ovato-oblonga.

**M. SCHLECHTENDALII**, Decaisne. Said to be Mexican as well as West Indian. The original was from St. Thomas, and has been recently distributed by Eggers.

gle, 104, 692. In habit between *G. parviflorus* and *G. pedunculatus*. But the crown is perfectly simple, with no internal crests or appendages, the margin abruptly produced into the five narrow and entire lobes which overtop the anthers, these of the firm texture which is common in the *Chthamalia* section, of which this species has wholly the aspect.

**GONOLOBUS CAUDATUS.** *Eugonolobus* quoad flores, habitu alieno, subglaber, suffruticoso-multicaulis e radice crassa; caulibus erectis vel subdiffusis ramosis foliosissimis; foliis e basi latiuscula nunc cuneata nunc truncata lanceolatis caudato-acuminatis infra medium undulatis pollicaribus, petiolo submarginato lin. 2-4 longo; pedunculis solitariis binisve brevissimis unifloris; sepalis linearibus; corolla rotata atrofusca crassiuscula 5-partita glabra, lobis lanceolato-subulatis (lin. 2 longis) eveniis; corona simplici annulari suberateriformi carnosio integro discum stigmatis cingente: folliculi desunt. — Gravelly soil, on the hacienda San José, about 25 miles south of Batopilas, *Palmer*, 75. The corona is quite entire or obscurely undulate, and has no internal appendages except perhaps five obscure lamellæ connecting it with the under side of the sessile stigma-disk.

**GONOLOBUS (CHTHAMALIA) ACUMINATUS.** *G. producto*, Torr., peraffinis; foliis pariter protracto-acuminatis atque folliculo (glaberrimo) longissime acuminato; corolla extus majus pubescente, fauce villosula; corona antheras superante 5-partita membranacea, lobis quasi ovato-quadratis apice lato-truncatis intus medio ligula brevissima ovata auctis (antheris haud adnatis). — Near Bachimba, 40 miles south of the city of Chihuahua, *Pringle*, 56. In some specimens of *G. producto* there is very slight adhesion of the lamellæ or ligulæ of the crown to the column under the anthers.

**GONOLOBUS (CHTHAMALIA) SCHAFFNERI**, Gray in Hemsl. Biol. Centr.-Am. Bot. ii. 334, and *G. bifidus*, Hemsl. l. c. 330, are manifestly the same species. The two names being of the same date, the first is rather to be preferred: the second is less appropriate, because the long ligules of the inner crown are not "bifid," except at the tip, perhaps not always even there.

**PHEROTRICHIS**, Decaisne, gen. *Asclep.-Gonolobearum* restitutum.

Calyx a basi 5-partitus, segmentis lanceolatis: glandulæ sinubus oppositæ solitariæ. Corolla campanulata, ultra medium 5-fida, crassiuscula: lobi in alabastro leviter contorto-obtegentes, ovati, intus pilis longis crebris primum retrorsis et medium versus inflexis comato-villosissimi, demum rotato-patentes. Corona ad juncturam columnæ brevis-

simæ et corollæ inserta, simplex, e squamis 5 planis obovato-quadratis apice exciso-truncatis constans, antheras superans. Antheræ tribi, sed prominentes, subcoriaceæ, latissimæ, stigmatis discum haud explanatum brevissime superantes, membrana oblonga tenui hyalina superatæ. Pollinia oblonga, horizontalia, curvula. Stigma umbone terminatum. Folliculi ovato-fusiformes. — Herbarum humiles, omnino erectæ, e radice crassa fusiformi vel tuberosa perennes, hirsutæ, foliosæ; foliis oppositis (paucisve alternis) oblongis utrinque obtusis penninerviis, imis nunc cordatis; floribus ad axillas umbellato-congestis, pedunculo brevissimo vel nullo. — *Pherotrichis*, Decaisne in Ann. Sci. Nat. ser. 2, ix. 322, & Endl. Gen. 1798; Gray, Syn. Fl. ii. (ed. 2), 462. *Lachnostomatis* sp., Decaisne in DC. Prodr. viii. 602.

P. BALBISII. Fusco-hirta; corollæ lobis acutiusculis intus sub lana venoso-reticulatis; coronæ squamis umbone angusto-conico stigmatis adæquantibus, apice latissime exciso quasi bilobo. — *Asclepias villosa*, Balbi in Mem. Acad. Turin, vii. 331, t. 4. *Cynanchum villosum*, Roem. & Schult. Syst. vi. 103. *Pherotrichis*, Decaisne, l. c. *Gonolobus pogonanthus*, Hemsl. Biol. Centr.-Am. Bot. ii. 333, quoad pl. Ghiesbreght. — Plant as to the original of the Turin Garden of unknown origin, but evidently the same as Ghiesbreght's no. 670, from Chiapas, S. Mexico. The umbo which surmounts the stigma is longer than all the rest of the gyno-andræcium, but is narrower at base than the disk which supports it. Balbi figures the follicles, which accord with those of the following species, and show some of the hairs which probably equally cover it when young.

P. SCHAFFNERI. Minus hirsuta; corollæ lobis obtusis, venis usque ad apicem nerviformibus simpliciusculis; coronæ squamis umbone maximo stigmatis subgloboso brevioribus, apicis truncati angulis vix productis; folliculis fusco-hirsutis demum glabrescentibus. — *Gonolobus pogonanthus*, Hemsl. l. c., quoad pl. Parry & Palmer. — San Luis Potosi, Northern Mexico, Schaffner, 63, Parry & Palmer, 586. S. W. Arizona, near Fort Huachuca, Lemmon, 2816.

This genus, which Decaisne partially indicated and afterwards suppressed, being now luckily identified and two species indicated, well merits restoration. It is certainly nearer to *Lachnostoma*, HBK., than to any part of *Gonolobus*. Yet the crown is not upon the corolla, as in the former genus, the very strongly bearded corolla-lobes and the stigma are quite peculiar, and moreover the plants are strictly erect, with the habit of *Asclepias* or *Acerates*. The anthers are appendaged with a distinct hyaline tip, which, however, would easily be overlooked.

*Gentianaceæ.*

*GENTIANA LANCEOLATA*, Griseb. in DC. Prodr. ix. 102. Grassy places in wet soil, on the mountain summits above Batopilas, at 8850 feet, *Palmer*, 361. A slender form, often simple-stemmed and one-flowered, from an annual root. Seed-coat minutely squamulose.

*GENTIANA WISLIZENI*, Engelm. Trans. Acad. St. Louis, ii. 215, t. 7. Same habitat as the preceding, *Palmer*, 334. Accords with the plant of Wislizenus.

*GENTIANA WRIGHTII*, Gray, Syn. Fl. ii. 118. Near Yerba Buena, at about 7,000 feet; the handsome white flowers with a yellowish tinge, *Palmer*, 306.

*GENTIANA ADSURGENS*, Cervantes in Griseb. Gent. 286. *G. angustifolia*, Hemsl. Biol. Centr.-Am. Bot. ii. 350, not Michx. Wet places on the mountain summits, at 8,850 feet, *Palmer*, 335. Apparently a common species in Mexico.

*HALENIA PARVIFLORA*, Don, answering to the var. *latifolia*, the short lower leaves being oval, which probably is the usual condition.\* Mountainous country, 150 miles north of Batopilas, *Palmer*, 403.

*HALENIA PALMERI*. Pedalis, striata, thyrsoido-pluriflora; foliis omnibus angusto-linearibus sub-uninerviis nonnullisve inferioribus subspathulatis fere trinerviis; floribus 4-meris semipollicaribus; sepalis lineari-lanceolatis; corollæ luteæ calcaribus pendulis subincurvis tenuisubulatis lin. 2-3 longis; capsula ultra-semipollicari. — Mountain summits above Batopilas, at 8,850 feet, *Palmer*, 359.

*Polemoniaceæ.*

*GILIA FLORIBUNDA*. Gray, Proc. Am. Acad. viii. 267. A condensed form, 150 miles north of Batopilas, *Palmer*, 398. Not before reported from Mexico.

*GILIA PRINGLEI*. *Ipomopsis*, sec. Gray, Syn. Fl. ii. (ed. 2), 410, inter *G. Thurberi* et *G. Macombii*. Perennis basi suffrutescente; foliis fere omnibus pinnatipartitis segmentis rhachique filiformibus molliibus; glomerulis florum laxiusculis; calycis lobis aristato-acuminatis; corolla pollicari violaceo-purpurea, tubo sursum sensim ampliato, lobis ovatis vel oblongis insigniter subulato-acuminatis; staminibus inæqualiter insertis fauce subinclusis, filamentis anthera oblonga haud

\* Ghiesbreght's no. 137 (we have not 618), referred to *H. parviflora* by Hemsl. with narrow linear leaves throughout, appears to be identical with the Quitensian *H. brevicornis*, Don.

longioribus: ovarii loculis 5-6-ovulatis; capsula calyce paullo brevior. — Hillsides west of the city of Chihuahua, Oct., *Pringle*, 559. Also W. Chihuahua about 150 miles north of Batopilas, *Palmer*, 431.

*Convolvulaceæ.*

JACQUEMONTIA PRINGLEI, Gray, Syn. Fl. ii. 434, var. GLABRESCENS. — Trailing or climbing over bushes, white-flowered, near Batopilas, *Palmer*, 107, 248. Appears to be essentially like the greener and glabrescent form of *J. Pringlei*, as collected by Pringle and also by Lemmon on the Mexican borders of Arizona; but somewhat larger-leaved, and the climbing form with rather many-flowered peduncles. Probably the genus were better merged in *Convolvulus*.

*Solanaceæ.*

PHYSALIS MICROPHYSA. Species singularis corolla per anthesin plano-rotata *P. lobata*, tamen calyce fructifero exangulato, pube simplici brevi parum viscida pubescens; caulibus pedilibus e radice perenni gracilibus paniculato-ramosis; foliis parvis (semipollicaribus) crenato-repandis, caulinis subrotundis pl. m. cordatis, ramealibus ovatis longiuscule petiolatis, floralibus diminutis; pedicellis calyce brevioribus; corolla (diam. semipoll.) ochroleuca maculis fusco-luteis; calyce sub anthesi lin. 2 longo in lobos lato-subulatos ultra medium usque fisso, fructifero ovato tereti lin. 5 longo, nervis inconspicuis, dentibus tubo brevioribus; seminibus crassiusculis immarginatis favoso-rugulosis. — Limestone cliffs, Santa Eulalia Mountains, near the city of Chihuahua, *Pringle*, 317. The late Mr. Miers, who did much work upon *Solanaceæ*, when describing a new species of the present genus, remarked that "all the species of *Physalis* are too well known and described to require any observation." We heartily wish they were.

*Scrophulariaceæ.*

PENTSTEMON COCCINEUS, Engelm. Pl. Wisl. 107. *Elmigeræ*; caule 1-2-pedali superne nudo gracili simplici vel subramoso racemoso-paucifloro (pedicellis gracilibus 1-2-bracteolatis sed unifloris); foliis linearibus imisve oblongis, summis setaceo-subulatis; corolla miniata *P. imberbis* sed magis ventricosa e tubo brevi angusto; antheræ loculis divaricatis modo *P. barbati*; filamentum sterili exserto apice subito dilatato nudo. (*P. barbatus*, var. *Wislizeni*, Gray, Proc. Am. Acad. vi. 59.) Var. FILIFOLIUS, foliis omnibus filiformibus vel angustissime linearibus; corolla demum violascente. — About 150 miles north of Batopilas, *Palmer*, 432. Not far from the district in which Dr. Wislizenus collected *P. coccineus*, Engelm., — a species to be restored,

although the name probably is not the most appropriate. Dr. Engelman noted the flowers as "bright scarlet or crimson"; the latter seemingly is the more correct. Dr. Palmer describes the corolla of his plant as "bronzy red, changing to bluish." The anther-cells at the line of dehiscence are sparsely spinulose-ciliate in Palmer's specimens; in those of Wislizenus, hardly at all so.

**PENTSTEMON FASCICULATUS.** Fruticulosus, pedalis, glaber, *P. pinifolio*, Greene, sat similis; ramis fastigiatis foliosissimis; foliis filiformibus seu acerosis rigidulis (circ. pollicaribus) oppositis confertis et in axillis fasciculatis, floralibus subulato-setaceis; racemo paucifloro, pedunculis inferioribus nunc bifloris; sepalis obovato-rotundis apiculatis; corolla coccinea ( $\frac{3}{4}$ -pollicari) tubulosa sursum sensim ampliata vix bilabiata, lobis 5 brevibus rotundato-ovatis subpatentibus; antheræ glabræ loculis demum explanatis suborbiculatis filamentoque sterili filiformi apice dilatato nudo e corolla haud exsertis. — At the Frailes, half-way between Batopilas and the Cumbre, or mountain summit, Palmer, 264.

**PENTSTEMON CAMPANULATUS**, Willd. At Yerba Buena, north of Batopilas, about 7,000 feet above sea-level, Palmer, 307. The most northern habitat known.

**STEMODIA PALMERI.** Inter *S. peduncularem* et *S. Jorullensem* collocanda, villosa, subviscosa, pedalis e radice annua? ramis diffusis; foliis oppositis (nec ternis) membranaceis longius petiolatis ovatis crenato- nunc duplicato-dentatis basi aut truncatis aut subcuneatis (lamina 6-10 et petiolo 3-5 lin. longa); pedunculis solitariis geminisve petiolo æquilongis; sepalis lineari-attenuatis corolla (lin. 5 longa) vix dimidio brevioribus; stigmatibus bilamellato vix infundibuliformi; placentis post dehisceniam apice bifido. — Shaded grounds, near Batopilas, Palmer, 221, the corolla purple with yellow throat; 250, with corolla white.

**SEYMERIA VIRGATA**, Benth. Coll. Pringle, 647. Besides this, which has by no means a virgate growth, Mr. Pringle collected specimens (567) referable to *S. pinnatisecta*, Seemann; and Palmer (325) another form on the higher mountains above Batopilas. The pubescence, foliage, and even the shape of the capsule, vary from specimen to specimen. Probably all of them (even the Texan one with short pedicels) belong to one polymorphous species.

**LAMOUROUXIA CORDATA**, Cham. & Schlecht. in Linnæa, v. 103.\*

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\* This name is retained, under the impression that the species is not to be merged in *L. viscosa*, HBK. Perhaps No. 703 of Ghiesbreght's Chiapas collec-

At the Frailes, above Batopilas, at over 7,000 feet: corolla (puberulent externally) said to be "bright carmine," *Palmer*, 258.

**LAMOUROUXIA COCCINEA.** *Hemispadon*, *L. cordata* soror, tantum puberula; foliis ovato-oblongis basi lata subcordata arcte sessilibus crebre serratis, superioribus spicas laterales sæpius fulcrantibus; calycis vix visciduli dentibus tubo haud longioribus; corolla læte coccinea tubulosa (nec ventricosa) sesquipollicari extus tenuissime puberula, labiis tubo dimidio brevioribus, galea oblonga recta; filamentis posticis tenuibus anantheris glabris; capsulis parvulis (lin. 4 longis) calyce fere inclusis. — Rocky hills near the city of Chihuahua, *Pringle*, 656.

**LAMOUROUXIA HYSSOPIFOLIA.** *L. longiflora* peraffinis, "frutescens tripedalis," sed ramis floridis gracilibus herbaceis foliosissimis; foliis spathulato-lanceolatis (majoribus vix ultra-pollicaribus), floralibus parvis; floribus patentissimis; calycis lobis tenui-subulatis tubo suo brevioribus; corolla miniata glabra antice ventricosa vix ultra-pollicari, galea lata spathacea obtusissima edentata. — At the Frailes in the mountains above Batopilas, at about 7,000 feet, *Palmer*, 260. Corolla said to be crimson, but seemingly pure red. — *L. longiflora* is not very well named, the corolla in our specimen from Hartweg being only an inch and a half long; in those of Seemann's collection hardly of that length, but rather more ventricose; in both the calyx-lobes are elongated and filiform. The present species has a more gibbous ventricose as well as smaller corolla, and the slightly recurved galea is not at all notched or toothed.

**CASTILLEIA MEXICANA.** *C. sessiliflora* proxima, hirsutula, corollæ ("ochroleucæ viridulo et roseo parum tinctæ") tubo prælongo labioque ampliori insignis. — *Orthocarpus Mexicanus*, Hemsl. Biol. Centr.-Am. Bot. ii. 463, t. 63, f. 1-6. — I see no good reason for referring this and the closely related *C. sessiliflora* to *Orthocarpus*; certainly none in any particular affinity with *Orthocarpus australis*. The lips of the corolla are no more nearly equal than in *C. pallida*; bifid calyx-lobes are common in the genus; and the lip of the corolla is not at all saccate in the present species. The elongated corolla-tube is, indeed, peculiar, but that is not particularly characteristic of *Orthocarpus*. Cool hillsides west of Chihuahua, *Pringle*, 209.

**PEDICULARIS ANGUSTIFOLIA**, Benth. Pl. Hartw. 22. Summit of the higher mountains above Batopilas, at 8,800 feet, *Palmer*, 326.

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tion is of still another species. The corollas are nearly two and a half inches long, completely cylindrical; the anthers extremely long-woolly, and the sterile filaments pubescent at and toward the apex.

Probably perennial, a foot high, freely branched; lowest leaves wanting; but all that are present are very narrow and simple, as in Hartweg's plant.

*Acantiaceæ.*

**CALOPHANES BILABIATA**, Seem. Bot. Herald, 324, t. 65. Hillsides near Batopilas, *Palmer*, 235. Although unusually bilabiate for this genus, the corolla-lobes (at least in Bourgeau's plant) are convolute in the bud.

**JUSTICIA CAUDATA**. *J. salviæflora*, HBK. affinis, sed præter pubem minutam foliorum et bractearum glabra; foliis ovatis summisve lanceolatis promissis caudato-acuminatis (majoribus 5-pollicaribus); corolla sesquipollicari ventricosa tubo incurvo antherisque glabris. — Shady ravines, near Batopilas, *Palmer*, 189. Seemann figures *J. salviæflora* (under *Sarotheca*, Nees), which he collected in the Sierra farther south, with corolla as well as calyx and bracts conspicuously glandular-pubescent, and anthers hirsute.

**JACOBINIA OVATA**. Fruticosa, effuse ramosa; foliis ovatis subacuminatis eximie penninerviis (sesquipollicaribus et petiolo lin. 3 longis) basi rotundatis supra viridibus puberulis subtus cum ramulis gracilibus mollissime pubescentibus subincanis; floribus subsolitariis paucisve; calycis alte 5-partiti segmentis linearibus acuminatis; corolla miniata puberula pollicari, labiis tubo angusto dimidio brevioribus, lobis angustis. — Shaded rocks near Batopilas, *Palmer*, 220. In pubescence and venation of the leaves somewhat like *J. incana*, the corolla more like that of *J. Mexicana*, Seem., from the same region; but in calyx, inflorescence, &c., very different from either.

**CARLOWRIGHTIA SERPYLLIFOLIA**. Suffrutex pedalis, tortuosoramosus, minute scabrido-puberulus; foliis parvis (cum petiolo lin. 3–4 longis) ovalibus ovatisque subnerviis (nunc triplinerviis); calycis segmentis setaceis stipiti capsulæ (sat valido eo æquilongo) adæquantibus; corolla purpurea. — Mountains near Jimulco, in Coahuila, *Pringle*, 218.

**CARLOWRIGHTIA ARIZONICA**, Gray, Proc. Am. Acad. xiii. 364, & Syn. Fl. ii. 327. Suffrutex ramosissimus, microphyllus; foliis subsessilibus oblongis lanceolatisque (lin. 2–4 longis) eveniis; calycis brevi segmentis subulatis stipite gracili (capsula longiore) 3–4-plo brevioribus. — This is here re-characterized from much more complete specimens than were before known, collected by Pringle in the mountains near Tucson, Arizona, and distributed in 1884.

**CARLOWRIGHTIA LINEARIFOLIA**, Gray, l. c., one of the original species, apparently as frutescent as the foregoing, and with filiform-linear

leaves, seems not to have been met with since its discovery by Mr. Wright in 1849. In all these species the anther-cells, though strictly parallel, are slightly oblique in position: there is no dilatation of the connective. The following is clearly a congener, and it takes with it the ambiguous *Dianthera parvifolia*.

**CARLOWRIGHTIA OVATA.** Caulibus herbaceis e caudice ligneo dif-fuso-procumbentibus fere glabris lævibusque gracilibus; foliis caulinis late ovatis acutis semipollicaribus penniveniis glabellis brevi-petiolatis, ramealibus ovato-lanceolatis, superioribus ad bracteas calyce tamen breviores reductis; corolla purpurea; calycis segmentis setaceo-subulatis stipitem capsulæ æquantibus; antheræ loculis brevi-ovalibus parum obliquis. — Rocky hills near the city of Chihuahua, *Pringle*, 995.

**CARLOWRIGHTIA PUBENS.** Caulibus fere herbaceis e caudice lig-nescente adsurgentibus cum foliis (ovatis obtusis paucivenosis petio-latis) pubescentibus vel hirsutulis; calycis segmentis subulato-setaceis stipitem capsula breviorē subæquantibus. — *Dianthera? parvifolia*, Gray, Syn. Fl. ii. 330; name inappropriate in the present genus. Rocky hills near the city of Chihuahua, *Pringle*, 65. Mr. Watson had suggested the reference of this plant to the present genus in Proc. Am. Acad. xviii. 133.

**CARLOWRIGHTIA CORDIFOLIA.** Glabra; caulibus e basi fruticulosa diffusis gracilibus; foliis majoribus dissitis membranaceis cordatis acutis pollicaribus et sesquipollicaribus cum petiolo gracili semipollicari; floribus secus ramos filiformes nudos laxè spicatis secundis; bracteis sepalisque minimis subulatis; corolla alba; antheræ loculis brevi-ovalibus contiguis æqualibus; stipite capsula æquilongò calyce bis superante. — On ledges in the mountains above Batopilas, *Palmer*, 224.

**ANISACANTHUS INSIGNIS**, Gray, Syn. Fl. ii. 457 (Suppl.), where the species are revised. — A fine species, formerly collected in Chihuahua by *Gregg*, later by *Palmer*, and now, in better specimens, by *Pringle*, 268. Dr. Havard found a form of it in the mountains on the Texan side of the Rio Grande. Mr. *Pringle* also collected one or two specimens of the true *A. virgularis*.

**HENRYA COSTATA.** Tenuiter pubescens, decumbens; foliis ovatis parvulis (haud ultrapollicaribus cum petioli lin. 1-3 longo) insigniter 10-14-costatis cuspidulatis; involucri bracteis mucronato-cuspidatis hinc connatis; corolla semipollicari, loculis antherarum elongato-oblongis inæqualibus. — Near Batopilas, pendent from precipitous rocks, *Palmer*, 211. It must be that *Henrya* of Nees is a good genus, and that this is a distinct species. The corolla is said to be straw-color.

*Verbenaceæ.*

*VITEX MOLLIS*, HBK.; Seem. Bot. Herald, 329, t. 71. Ravines near Batopilas, *Palmer*, with mature fruit, which seems to have been nearly unknown. Seemann, indeed, gives the character "capsula obovato-rotundata glabra," but the specimen figured is in flower only. The fruit now in hand is a globose drupe, half an inch or more in diameter, with thin pulp and a very thick bony putamen. Dr. Palmer notes that the fruit, called *Uvalama*, is eaten by the Indians, either raw or cooked.

*Labiataæ.*

*HYPTIS SEEMANNI*. Facie *H. stellulata*, Benth., pube molliori tomentoso-canescens; caule herbaceo orgyali; foliis oblongo-lanceolatis rugulosis crebriter crenulatis basi rotundatis (2-3-pollicaribus cum petiolo subsemipollicari); capitulis seu verticillastris globosis modo *H. stellulata* concatenatis; bracteis subulatis minimis deciduis; calyce obconico (etiam fructifero haud ultra lineam longo), dentibus subulatis erectis mollibus tubo villosissimo dimidio brevioribus intus fauceque lanosissimis; corolla parum exserta. — N. W. Mexico, probably the species merely mentioned from "Cerro de Pinal," *Seemann*. Mountain-sides above Batopilas, *Palmer*, 177.

*HEDEOMA COSTATA*, Gray, Syn. Fl. ii. 363, 1878; Hemsl. Biol. Centr.-Am. ii. 547, 1882, where by oversight it is taken up as original. — Mountains near the city of Chihuahua, *Pringle*, 133. Near Batopilas, *Palmer*, 441. So this species has a wide range in Mexico, and Dr. Havard found it in the mountains on the Texan side of the Rio Grande, but in forms which too nearly approach *H. plicata* and *H. dentata*.

*SALVIA TILLEFOLIA*, Vahl. This common weed in Mexico is, according to Dr. Palmer, the *Chia* of the district he visited, the seeds of which are largely infused for a mucilaginous drink, as is done in Arizona and California with *S. Columbariæ*.

*SALVIA MICROPHYLLA*, HBK., Nov. Gen. & Spec. ii. 295. The plants here referred (including 748, 739, *Parry & Palmer*, and 662, *Schaffner*) very well accord with the original character, except as to degree of pubescence, having at most a trace of "calycibus hirtis," but coming near to Bentham's "nervis pubescentibus," and they do seem to run into the larger-leaved *S. Grahami*, Benth.

Var. *CANESCENS*, Gray in Distrib. *Pringle*, may be near the original, as it is the most pubescent form, and the rugose small leaves are densely

canescently pubescent on both sides. — Hills near Zacatecas, *Pringle*, 239. Some of Parry and Palmer's 739 come very near to it, and have hirsute pubescence on the branchlets.

Var. *WISLIZENI* is more herbaceous and greener, merely puberulent, but the calyx-nerves are more obviously hispidulous, the small leaves less crenulate and not rugulose. — Sierra Madre west of Chihuahua, *Wislizenus*, 152. Not far south of this, i. e. 150 miles north of Batopilas, *Palmer*, 379.

*SALVIA LYCIOIDES*. *Calosplax*, frutescens, viridis, sub lente minutissime puberula; ramis gracilibus elongatis foliosis; foliis parvis (majoribus semipollicaribus) angusto-oblongis obtusis integerrimis raro paucidenticulatis basi contracta subpetiolatis, venis obscuris, floralibus minimis caducis; verticillastris 2-4-floris; corolla semipollicari cærulea calyce triplo longiore sub fauce ventricosa glabra, labio postico oblongo apice puberulo, antico parum longiore rotundato trilobo. — Santa Eulalia Mountains, near the city of Chihuahua, *Pringle*, 52. I know no species with which this may be particularly compared. The foliage might be likened to that of a *Lycium*; whence the name.

*SALVIA ALBIFLORA*, Mart. & Gal., at least the plant so named in Mex. Bound. Survey, from the Mexican border. Shady ravines near Batopilas, *Palmer*, 154. Forma *CÆRULESCENS*, with "corolla light blue, often almost white when in shade," *Palmer*, 96; also "bright blue in shady ravines," *Palmer*, 157. Since Linden records the color of the corolla in his specimens as pale blue, we may safely refer all of *Palmer's* to one species. Seemann's plant referred to *S. flexuosa* differs only in a slightly larger calyx.

*SALVIA PALMERI*. Herbaceæ, suborgyalis, *S. polystachyæ* peraffinis, thyrsos pariter contracto densifloro; foliis ovatis rarius subcordatis tantum serrulatis haud rugoso-venosis supra viridibus fere glabris subtus incanis; stylo nudo vel parce pilosulo. — Hillsides at the Frailes, on the mountains above Batopilas; blue-flowered, *Palmer*, 259. The difference in hue between the two faces of the leaf is striking, especially in the younger leaves; the whiteness of the lower face, unlike that of *S. polystachya*, is from a pubescence too minute and close to be distinguished into separate hairs, even with a lens, and is persistent.

*CEDRONELLA MICRANTHA*, Gray. About 150 miles north of Batopilas, *Palmer*, 420, with the same minute corollas before known.

*CEDRONELLA AURANTIACA*. Puberulo-incana; foliis deltoideo-lanceolatis vel subhastatis subcrenatis (1-2-pollicaribus cum petiolo  $\frac{1}{4}$ -pollicari) supra viridibus subtus canis; thyrsos superne nudo laxifloro; calyce campanulato fere herbaceo (lin. 2 longo), dentibus deltoi-

*deis obtusiusculis*, duobus paullo brevioribus; corolla ultrapollicari pallide aurantiaca ea *C. Mexicanæ* referente sed inferne magis attenuata.—Ravines 150 miles north of Batopilas, *Palmer*, 402. Singular in the color of the corolla, which, if not yellow, is "salmon-color," as well as in the short and broad-toothed calyx.

### 3. *Miscellanea.*

#### SIDALCEA.

M. Alphonse De Candolle, in the Preface to the "Calques des Dessins de la Flore du Mexique de Mocino et Sessé," several years ago pointed out the fact that the original *Sida malvæflora*, DC., was not the plant of the Botanical Register, and not the plant taken up by me as *Sidalcea malvæflora*. Also I had recognized Mocino's drawing to belong to what I had named *Sidalcea humilis*, the common species of the Californian coast; but I had deferred calling attention to it until I could revise the whole genus and rectify the synonymy. In consequence of this inadvertence Mr. Greene did not know of this correction when he published his revision of *Sidalcea*, a year or more ago. For the present it suffices to note that the name SIDALCEA MALVÆFLORA belongs to the *Sida malvæflora*, Hook. & Arn., &c., and has *Sidalcea humilis*, Gray, Pl. Fendl., for a synonym; while the other names, *S. Neomexicana* and *S. Oregana* of Pl. Fendlerianæ, come into use for the interior-country species.

Two of the annual species which, in the Botany of California, Mr. Watson inadvertently combined, are quite distinct, and were fairly well characterized in the original account of the genus, viz. *S. Hartwegi* and *S. hirsuta*. A year ago I found them growing near each other, in exsiccated pond-holes or pieces of depressed ground in grain-fields, on the Rancho Chico of the esteemed Gen. John Bidwell, where, as I suppose, Hartweg found them. The former also grows on elevated ground along the borders of Chico Cañon.

*S. HARTWEGI*, Gray, Pl. Fendl. 20, & in Pl. Hartw. 300, is slender and much smaller than the other; with only fine and short pubescence on the higher parts, loosely and paniculately branching, and sparsely flowered; the corolla of a deep pink purple and from one third to two thirds of an inch long. The carpels are whole and closed when they separate from the axis, are strongly reniform-incurved or with basal portion straighter, the whole of the firm dorsal portion strongly rugose-reticulated, the rugæ sharp and salient, especially on

the sides; the soft apiculation inconspicuous and at length deciduous. Hartweg's specimens are small, few-flowered, and not in fruit. Without much doubt the *S. tenella* of Greene, from the Little Chico Creek, is a depauperate and very branching form of *S. Hartwegi*, with flowers much reduced in size. Prof. Rattan collected specimens on Stony Creek, Colusa Co., which are fairly intermediate.

*S. HIRSUTA*, Gray, Pl. Wright. i. 16, (which in Pl. Fendl. and Pl. Hartw. I mistook for Nuttall's *Sida delphinifolia*,) is stout, taller, with more or less hirsute pubescence; the stem and erect branches terminated with a dense spike or spiciform cluster of flowers; the corolla more rose-colored, from three fourths to nearly a full inch long. The carpels were very well described long ago in Pl. Fendl., and well figured in my Genera Illustrated. They are not sensibly incurved, are surmounted by a conspicuous soft and hairy beak, the thin ventral portion tears open on separation from the receptacle, and the back is lightly reticulated.

*S. CALYCOSA*, of Marcus E. Jones in the American Naturalist, from Duncan's Mills, on Russian River, is a badly named but apparently good species, nearly allied to the preceding. Its calyx-lobes are broader, shorter, and hirsutely long-ciliate; the carpels are striately nervose on the back (the reticulations being very long and narrow); and the apiculation is apparently obsolete. This proves to be the *S. sulcata* of Curran, fide Greene in Bull. Calif. Acad. i. 79, a better name.

*S. DIPLOSCYPHA*, Gray, the remaining species of the group, is not to be confounded with any other; but the variety, *minor*, seems to be well marked. This species and *S. hirsuta* ought to be in ornamental cultivation.

#### LYONOTHAMNUS, Gray, Proc. Am. Acad. xx. 291.

Char. fruct. Folliculi 2 (rarissime 3) parvi, ovati, stylo brevi demum deciduo mutici, crasso-coriacei, glandulis substipitatis scabrati, sutura ventrali (demumque dorsali?) dehiscentes. Semina (1 vel 2 maturescentia) elongato-oblonga, parum arcuata; testa membranacea secus raphen anguste alato-marginata. Embryo (vix matura) in albumine parco inclusus, leviter arcuatus; radícula supera cotyledonibus oblongis paullo brevior.

LYONOTHAMNUS FLORIBUNDUS, Gray, l. c. Upon revisiting the island of Santa Catalina in the early part of the summer of 1885, Mr. Lyon collected specimens of this interesting shrub, with forming fruit, not quite mature indeed, but enough so to furnish a few seeds with a

full-grown embryo. Having waited in vain for better material, I now give the carpological characters, drawn from what we possess.

**LYONOTHAMNUS ASPLENIFOLIUS**, Greene, Bull. Calif. Acad. i. 187. Folia pinnatisecta in segmenta 3-5 approximata lato-linearia pinnatipartita, lobis crebris semilunato-deltoides. — Faint indications of stipules are seen in this species, of which the known materials are still imperfect. It is hoped that Santa Cruz Island, off Santa Barbara, and the other islands of that coast, may soon be explored.

This is another of those genera which tend to obliterate the distinctions between the *Rosaceæ* and the *Saxifragaceæ*. Notwithstanding the likeness to *Vauquelinia*, I still incline to refer this genus to the latter order (next to *Jamesia* and *Fendlera*), on account of the opposite leaves, dicarpellary ovary, and albuminous seeds, although indeed the albumen is thin. *Vauquelinia* is obviously Rosaceous. Both the species (*V. corymbosa* and *V. Torreyi*) not rarely show minute adnate stipules to their alternate leaves; and they have more than "two" — at least four — ovules in each cell of the 5-merous and syncarpous ovary, all ascending from next the base of the cell. The seeds have an apical wing, as figured, and are completely exalbuminous, the broad and flat cotyledons filling the seed-coat completely.

The following has already been published in a Supplement to a second issue of the Synoptical Flora (pp. 448, 449); but it is thought best still to print here the original description.

**DIMERESIA**, Nov. Gen. *Comp.-Inuloidearum*.

Capitula biflora, discreta, homogama. Involucrum diphyllum; bracteis herbaceis oblongis basi tantum connatis, utrisque florem hermaphroditum fere amplexantibus. Corollæ tubulosæ, regulares, 5-dentatæ. Antheræ basi breviter caudato-sagittatæ. Styli rami angusto-lineares, obtusi, ad apicem usque lineis stigmaticis marginati. Achenia clavato-pyriformia, multistriata, glabra, areola epigyna parva. Pappus e setis 20 validis plumosis uniseriatis basi in annulum connatis, mox deciduus. — Herbula annua, depressa, vix caulescens, glabrata; foliis rosulato-confertis crassiusculis obovatis integerrimis 3-5-nervatis basi in petiolum marginatum angustatis; capitulis subsessilibus plurimis inter folia congestis; floribus ut videtur albidis.

**DIMERESIA HOWELLII**. — On Stein's Mountain, in southeastern part of Oregon, June, 1885, *Thomas Howell*. Also received, since this account was written, from *W. C. Cusick*, who found it a little later in the same district. — A singular little plant, named from the two-flowered heads, with involucre reduced to two bracts, one sub-

tending each flower. Not obviously of near relationship to any other known genus; but clearly of the tribe *Inuloideæ* by the style and anthers, although it does not fall well into any of the characterized subtribes. Yet it is most like the *Angiantheæ*.

ASTRAGALUS NEVINII. *A. Drummondii* et *A. racemoso* ut videtur parum affinis, pube brevi adpressa canescens; foliis plurimis oblongis retusis; pedunculo subcapitato-plurifloro; calycis nigricantis dentibus tubo campanulato paullo brevioribus; corolla (vix evoluta) alba; leguminibus patentibus glabris tenuiter transversim reticulatis oblongis arcuatis utrinque subacutis dorso late sulcato intrusis bilocellatis ventre acutatis (sectione transversa latissime Y-formi) in stipitem calyce bis superantem repente contractis.—Island of San Clemente, off Southern California, Messrs. *Nevin* and *Lyon*, April, 1885. Apparently a low species, with stems only a foot high.

SOLIDAGO ERECTA, Pursh. The proper reference of this obscure species was inadvertently omitted from the Synoptical Flora, even from the recent Supplement. So it may here be recorded that no specimen bearing this name can be found in the Banksian herbarium. But there is a "*S. stricta*  $\beta$ , Mss." which answers the conditions. This appears to be the *S. bicolor*, var. *concolor*, of the Flora; and so *S. erecta* may be the proper name for this ambiguous Golden-rod, if (as is probable) it comes to be recognized as a species. *S. erecta* of Elliott may be the smoother form of it.

SOLIDAGO ELATA, Pursh, also should have been more definitely referred to in the Syn. Flora. The three sheets of it in the Banksian herbarium seem to belong to as many species. The first, a specimen from a cultivated plant, seemed to me to be *S. sempervirens*, var. *viminea*. The second, from "New Jersey, Bartram," has the panicle abnormally branched through an early injury to the summit of the stem. I took it probably to be the *S. bicolor*, var. *concolor*. The third, "*S. elata*, Mss. & herb. Miller," apparently from a cultivated plant, seemed to be a form of the European *S. Virgaurea*.

LESSINGIA LEMMONI. *L. Germanorum* sat similis, magis robusta; indumento tenuiore; capitulis paullo majoribus; corollis luteis, exterioribus limbo ampliato; styli ramis in cuspidem subulatam longe productis; acheniis turbinatis albo-villosissimis; pappo multisetoso subæquali.—At Ash Fork, in northern part of Arizona, *Lemmon*.—This species requires a modification of the character of the first section of the genus in the Syn. Fl. i.<sup>2</sup> 162, as to the style-appendages, which are like those of the white- and purple-flowered section. And the species is more eastern than any other.

**HELIANTHUS CUSICKII.** *H. Nuttallii* et *H. gracilentii* parum affinis, multicaulis e caudice crasso perpendiculari resinifero, strigulosus, sæpe hispidulus; caulibus ultrapedalibus ramisve monocephalis demum reclinatis; foliis plerisque alternis lineari- seu angusto-lanceolatis integerrimis obtusiusculis basi attenuata sessilibus leviter trinervatis fere eveniis; involucri (vix ultra-semipollicaris) bracteis angusto-lanceolatis sensim acuminatis hirtociliatis demum laxis; ligulis (1-1½-pollicaribus) elongatis; acheniis glaberrimis; pappi paleis oblongo-lanceolatis majusculis, squamellis nullis. — A very marked species, of the Desert region, first received from Mr. Cusick, then from Mr. Brandegee. On dry hills near the Malheur River, S. E. Oregon, coll. in early summer of 1885, in flower, *Cusick*. "Has thick and succulent roots, an inch or two in diameter, of a sweetish taste." Among sage-brush, in the northern Yakima region, Washington Terr., Oct., 1885, *Brandegee*, with flower and fruit, "forming clumps, the many stems at length resting on the ground in an entangled mass."

**ARTEMISIA PYGMÆA.** *Scriphidium*, fruticulosa, spithamæa e caudice crasso lignoso, multicaulis, tenuiter canescens, demum glabrata; foliis (lin. 2-5 longis) rigidulis pinnati-3-7-partitis, segmentis subulato-linearibus obtusiusculis; capitulis spicatis folio fulcrante longioribus; involucreo cylindraceo (lin. 2-3 longo), bracteis pluriseriatis lineari-oblongis glabellis chartaceis margine scariosis, inferioribus dorso crassiore viridulo; floribus 3-4 et achenio (immature) glabris. — Desert region of Nevada, at Fisk Creek near Eureka, *Brandegee*, August, 1885.

**ECHINOSPERMUM BRACHYCENTRUM**, Ledeb. Fl. Alt., & Ic. Fl. Ross. iv. t. 302. — Var. **BRACHYSTYLUM**. — Spence's Bridge, Thompson River, Brit. Columbia, *J. Fletcher*, fide *Macoun*. — A low and villous-hirsute leafy-bracteate species, but the bracts short; the nutlets convex on the back within the low callous margin, which bears scattered lightly glochidiate papillæ or extremely short setæ (or even these sometimes obsolete), and is not at all carinate. Our plant accords well with Ledebour's figure, except that the style is not exerted beyond the apex of the nutlets.

**MIRABILIS BIGELOVII.** Viscosissimum, villosum, caulibus foliisque rotundatis flaccidis; perianthio pallido involucrum parum superante; cæt. fere *M. Californicæ*. — *Oxybaphus glabrifolius*, Torr. Pacif. R. R. Exp. iv. 131, quoad pl. Colorad. valde pubescens. — Arizona, and perhaps in California on the Colorado. Common in the Grand Cañon of the Colorado, below Peach Spring, collected May 5, 1885, *A. G.*

## XXIV.

## CONTRIBUTIONS TO AMERICAN BOTANY.

BY SERENO WATSON.

Communicated April 14, 1886.

1. *List of Plants collected by Dr. Edward Palmer in Southwestern Chihuahua, Mexico, in 1885.*

THE very interesting collection of plants of which a list is here given was made in the Sierra Madre, in the southwestern portion of the province of Chihuahua, and chiefly in the neighborhood of the mining town of Batopilas. The particular localities given by Dr. Palmer are Hacienda San Miguel, one mile from Batopilas, at an altitude of 2,400 feet above the sea, and Hacienda San Jose, about twenty-five miles distant southward and at a considerably lower elevation, both these places being upon the Batopilas River, which flows through a very contracted valley, the steep rocky mountain slopes and spurs coming down so close to the stream that even a mule track is barely possible along its course; Cumbre, on the summit of the mountains above Batopilas, at an elevation of 8,850 feet; Frayles, intermediate between Cumbre and Batopilas, alt. 7,000 feet; Yerba Buena, a similar locality at the same altitude; and Norogachi, an Indian village about 150 miles north of Batopilas, at about 8,500 feet altitude. These latter places are in a rough broken region, intersected by numerous ridges and ravines and surrounded at no great distance by high mountain peaks, more or less covered by pines and oaks, with occasional grassy openings. A considerable amount of snow falls here in winter, and a comparatively low temperature is reached. The collections at the haciendas were made mostly in August and September, at Cumbre and Frayles in October, at Yerba Buena and Norogachi, in November. The determinations of the gamopetalous species were made by Dr. Gray, of the *Cyperaceæ* by Dr. N. L. Britton, of the *Gramineæ* by Dr. George Vasey, and of the cryptogams by Prof. D. C. Eaton. The numbers and letters in parentheses are those under which the collection has been distributed.

**AQUILEGIA SKINNERI**, Hook. Identical with the plant figured in Bot. Mag. (1842), t. 3919, which is said to have been raised from seeds collected in Guatemala by G. U. Skinner. It would seem that the plant itself has never before been collected, either in Guatemala or elsewhere. As it has proved to be perfectly hardy in the gardens of England, a tropical habitat is not probable, especially as the genus otherwise is confined to temperate regions. — Cumbre (336).

**DELPHINIUM LEPTOPHYLLUM**, Hemsl. The claws of the lateral petals, however, have an appendage at base, the absence of which is made a characteristic difference between this species and *D. pedatisectum*, Hemsl. Possibly the two species are not distinct. — Norogachi (424).

**SISYMBRIUM INCISUM**, Engelm. — Norogachi (421).

**CLEOME (PHYSOSTEMON) MELANOSPERMA**. Annual, slender, erect and branching, two feet high, glabrous or very slightly puberulent: leaves trifoliate, the thin leaflets lanceolate to narrowly lanceolate, more or less acuminate, mostly cuneate at base, the blade (1 or 2 inches long) exceeding the petiole; the uppermost floral leaves simple, linear-lanceolate and sessile: pedicels slender, exceeding the bracts: sepals distinct, linear; petals "creamy white," 3 or 4 lines long: capsule narrowly oblong (8 or 9 lines long), attenuate at each end, the stipe about three lines long: seed dull black, irregularly undulate-reticulate. — Hacienda San Miguel (94).

**IONIDIUM PARIETARÆFOLIUM**, DC.? A slender erect branching annual, the stem and branches somewhat villous, and with a line of dense pubescence: some of the lower leaves opposite, all lanceolate, acute or acuminate, mostly narrowed to a slender base, bluntly serrate, nearly glabrous, 1 to 2½ inches long: pedicels 4 to 6 lines long, or in the main axils an inch long: lower petal white or purplish, four lines long, the upper tipped with dark purple. — Haciendas San Miguel (93) and San Jose (25). Resembling 2661 Bourgeau, 35 Bili-mek, and 472 Botteri, all from Orizaba, as well as specimens collected by Purdie and Holton in New Grenada, and by Fendler (2419) in Venezuela, except that these are all not villous and have the leaves more acutely serrate. Mr. Hemsley refers this species to *I. riparium*, HBK., but Eichler identifies this last with *I. oppositifolium*, leaving De Candolle's species distinct. 859 Wright, from Sonora (*I. riparium*, var., Gray, Pl. Wright. 2. 16), in fruit, is not villous, and has the capsules nearly sessile and sometimes subfascicled in the axils.

**AMOREUXIA PALMATIFIDA**, DC. (*A. Schiedeana*, Planch.) — Hacienda San Miguel (Q).

**POLYGALA BERLANDIERI.** A slender puberulent annual, branching above, 2 to 6 inches high: leaves linear, acuminate, alternate or a few of the lowermost opposite or verticillate, 4 to 8 lines long: raceme sessile or nearly so, loosely flowered, an inch becoming 2 or 3 inches long: flowers white or pale pink, reflexed, the oblong obtuse petals three fourths of a line long: capsule twice longer, narrowly oblong: seed straight, cylindrical, acute at base with the short conical silky caruncle, which is very shortly appendaged; pubescence appressed-villous, the upper hairs longer and extending beyond the top of the seed. — Cumbre (323). Also collected by Berlandier (n. 721, 2138), in November, 1830, at Sacahuales in the mountains of southern Tamaulipas between Tula and Tampico, and by Botteri at Orizaba (n. 1119, in herb. Gray).

**POLYGALA ALBA**, Nutt., var. (?) **SUSPECTA.** Annual, or sometimes biennial, with mostly decumbent stems (2 inches to a foot high) and verticillate oblanceolate leaves, the upper narrower and alternate: racemes shortly pedunculate or nearly sessile: petals more or less tinged with pink: seed oblong-obovate, thinly appressed-pubescent, with a somewhat cucullate oblique pubescent caruncle, and lateral appendages half the length of the seed. — Norogachi (369). Apparently common in northern Mexico, having been collected near San Luis Potosi by Schaffner (4, 5) and Parry & Palmer (39), at San Antonio de las Alanzanes by Dr. Gregg (371), in the Sierra Madre by Seemann, in Sonora by Wright, and in southern Arizona by Lemmon.

Typical *P. alba* appears to be biennial or perennial, with taller ascending stems, the leaves usually all narrower and rarely at all verticillate, the racemes long-pedunculate, with white or green-nerved flowers (2 lines long), and oblong-elliptical capsules: seed oblong-obovate, covered with closely appressed silky hairs, with a prominent oblique glabrous or slightly pubescent cucullate caruncle, the lateral appendages half as long as the seed. It ranges from the Upper Missouri and Kansas to Texas, New Mexico, and northern Mexico (725 Coulter; 30 Hartweg; 1092 Thurber; 68 Palmer). It has not been found east of the Mississippi, Buckley's specimens from Alabama, which have been referred to it, being a narrow-leaved form of *P. Boykinii*.

Of the species allied to *P. alba*, the perennial *P. SCOPARIA* has a narrowly elliptical capsule, and a straight linear seed ( $1\frac{1}{3}$  lines long) covered with subappressed villous pubescence (not retrorse, as originally described), with a slightly prominent oblique caruncle, the contiguous appendages more than half the length of the seed. *P. BOYKINII*,

a biennial or perennial, with numerous nearly erect stems 1 or 2 feet high, has a round-elliptical capsule, and a curved oblong seed densely covered with loosely appressed hairs, a rounded pubescent caruncle pitted on the inner side, and the lateral appendages half as long as the seed. There are no specimens in herb. Gray from west of the Mississippi; it has been credited to Mexico and Guatemala, but probably erroneously. *P. bicolor*, HBK., is usually referred as a synonym to *P. alba*, but by Hemsley to *P. Boykinii*. The flowers are scarcely more than half the size of those of *P. alba* and are reddish when dried. The reference even to *P. alba* may still be considered doubtful.

**KRAMERIA BICOLOR.** A shrub, 3 to 5 feet high, with green bark, the younger branches covered with a dense spreading pubescence: leaves oblong-lanceolate to linear, sessile, 4 to 8 lines long, short-villous above, the hairs beneath longer and silky: pedicels axillary, bibracteolate: sepals acuminate, 3 to 5 lines long; petals and stamens free, the lower fleshy tuberculate petals about equalling the upper, orbicular,  $1\frac{1}{2}$  lines long; claws of the upper petals green and thickened, the limb purple, the middle one slightly dilated, the outer obliquely reniform: fruit globose, 4 lines broad, densely covered with spreading hairs and armed with rather stout glochidiolate prickles. — Hacienda San Jose (37). Differing from *K. canescens* especially in its pubescence, petals, and the stouter prickles of the fruit.

**DRYMARIA TENELLA**, Gray. — Same locality (59).

**PORTULACA PILOSA**, Linn. ?, with submoniliform tuberous roots. — Same locality (79).

**FOUQUIERA SPINOSA**, HBK. ? — Hacienda San Miguel (228). Like Sonora specimens collected by Thurber, but the panicle more open and the pedicels longer than shown in the original figure.

**MALVASTRUM TRICUSPIDATUM**, Gray, var. **BICUSPIDATUM**. The ventral cusp of the carpel obsolete; shrubby, the flowers opening at night. — Same locality (8).

**MALVASTRUM JACENS.** Annual, decumbent or nearly prostrate, the stems and petioles stellate-pubescent and hispid with spreading sub-fascicled hairs: leaves triangular-ovate to round-reniform, truncate at base, 3-5-lobed, irregularly laciniate-crenate, 1 or 2 inches long, the floral much smaller: flowers on short slender pedicels in the axils of the stem or of short branches; calyx cleft to below the middle, with filiform bractlets; petals purplish, equalling the calyx (2 lines long): carpels 8, depressed and rounded, not beaked, strongly rugose. — Norogachi (430); also 90 Parry & Palmer, from near San Luis Potosi.

*ANODA HASTATA*, Cav. The carpels not crested. — Hacienda San Miguel (234).

*ANODA PARVIFLORA*, Cav. — Same locality (128).

*ABUTILON REVENTUM*. Tall and erect, the stem glabrous or slightly puberulent: leaves round-cordate with closed sinus, acuminate and with small obtuse irregular teeth, densely covered on both sides with a very soft velvety pubescence, whiter beneath, 4 to 6 inches long, about equalling the petioles: flowers in a large open panicle, on pedicels (an inch long or less) jointed above the middle: calyx velvety, cleft to below the middle, the ovate lobes acute; petals deep orange, 6 lines long, twice longer than the calyx: carpels (about 8) finely stellate-pubescent, oblong, rounded at the top or obscurely cuspidate, 4 lines long. — Hacienda San Jose (56); first collected by Thurber near Ures in Sonora (*A. Sonoræ*, var., Gray in Pl. Thurb. 308), and recently by Pringle (n. 27, of 1882) in the Santa Catalina Mountains of Arizona, distributed under the same name.

*ABUTILON SONORÆ*, Gray. — Hacienda San Miguel (171).

*ABUTILON HYPOLEUCUM*, Gray, var.? The pubescence of the lower side of the leaves and on the petioles densely stellate instead of velutinous, and the veins prominent. — Same locality (172).

*ABUTILON CRISPUM*, Don. A very villous form. — Same locality (173).

*HIBISCUS COULTERI*, Gray. — Same locality (90).

*HIBISCUS PHŒNICEUS*, Jacq., var. The calyx-lobes shorter and more acuminate; a shrub, 10 feet high. — Same locality (242).

*HIBISCUS (KETMIA) BISEPTUS*. Stem, branches, petioles and involucre hispid with brownish spreading hairs: leaves thin, rounded ovate, truncate or subcordate at base, mostly 3-5-lobed to the middle with ovate acute and coarsely toothed lobes, thinly covered with appressed hairs which on the under side are 3-forked and above simple or 2-forked, 4 inches long or less, exceeding the petioles: pedicels solitary, axillary, exceeding the leaves: involucre of ten linear bracts, 12 to 15 lines long; calyx cleft nearly to the base, the lanceolate acuminate lobes equalling the involucre; petals "white" with a dark purple base, nearly two inches long; filaments purple; pollen deep orange-color. — Same locality (3). Not in fruit.

*INGENHOUSIA TRILOBA*, DC. — Frayles (269).

*ERIODENDRON ACUMINATUM*. A wide-spreading tree, 20 feet high by one to two feet in diameter, the young unarmed branches and base of the petioles (3 or 4 inches long) finely pubescent: leaflets 5 to 7, thin, oblanceolate, narrowly acuminate, narrowed below to a short

pubescent petiolule, very acutely laciniate-denticulate, sparsely pubescent above, subtomentose beneath, 2 to 4 inches long: fruit 6 inches long, oblong: seed obovate, nearly 4 lines long, the narrow rhaps prominent; radicle inflexed. — Hacienda San Miguel (F). Perhaps the same that was collected by Moçino & Sessé (Icon. t. 94), referred by De Candolle to *E. asculifolium*, a species from the coast of Campeche. The petals of the latter are described as about five inches long, very much longer than those of the figure given by Moçino & Sessé, nor does the description accord in other respects with the present specimens. The figure of Moçino & Sessé represents a short branch, armed in part with short recurved prickles, with leaflets like Palmer's, but less acuminate; the pedicels are very short and stout, terminal upon very short branchlets; flowers pubescent, the calyx tubular (8 or 9 lines long) with broad ovate teeth, the petals ( $2\frac{1}{2}$  inches long) about equalling the five stamens.

**WALTHERIA DETONSA**, Gray. Flowers opening in the evening. — Hacienda San Miguel (20).

**GUAZUMA TOMENTOSA**, HBK. A tree 15 to 20 feet high and one or two in diameter, with soft white wood, used for making spoons and other articles. The bark is made into ropes, and the inner part of the fruit with the seeds is sometimes ground and made into cakes. — Same locality (J). Known as "Guacima" or "Mexican elm."

**AYENIA FUSILLA**, Linn. — Same locality (21).

**AYENIA BERLANDIERI**. Suffrutescent, 3 to 6 feet high, densely pubescent: leaves broadly ovate to lanceolate, acute or often shortly acuminate, subcordate or rounded at base, coarsely serrate, sometimes obscurely 3-lobed, densely stellate-tomentose beneath, at least when young, much smoother above, 2 or 3 inches long or more, the petioles 6 to 12 lines long: peduncles fascicled in the axils, shorter than the petioles, the umbels 3-5-flowered: flowers purplish brown, small, the lanceolate acuminate sepals  $1\frac{1}{2}$  lines long; blade of the petals 2-parted, the lobes parallel: anthers 2-celled: ovary pubescent; fruit 3 or 4 lines broad, on pedicels 3 to 5 lines long. — Same locality (19, 83); also found by Berlandier in 1830 (n. 788, 2208) near Santander and at San Rafael in Tamaulipas.

**AYENIA PALMERI**. Suffrutescent, about 5 feet high, densely pubescent: leaves on petioles 1 to 6 lines long, ovate, acute, subcordate at base, occasionally obscurely 3-lobed, rather finely serrate, stellate-tomentose beneath, smoother above, 1 or 2 inches long: peduncles fascicled, slender, short, 1-3-flowered: flowers greenish, small, the lanceolate acuminate sepals  $1\frac{1}{2}$  lines long; blade of the petals lunate:

anthers 3-celled: ovary pubescent; fruit 3 lines broad, on very slender pedicels 4 lines long. — Same locality (179, 180).

**TRIUMFETTA GALEOTTIANA**, Turcz.? Suffrutescent, with slender branches, finely stellate-pubescent: leaves finely pubescent, whiter and more tomentose beneath, ovate or the upper lanceolate, narrowly acuminate, very unequally toothed, the larger slightly 3-lobed, rounded or subcordate at base, 1 or 2 inches long: flowers on short axillary peduncles and in a terminal raceme; sepals 2 to 4 lines long, finely pubescent, with slender appendages; petals narrowly oblanceolate: stamens 20: ovary 3-celled, nearly equalling the petals. — Same locality (23). Nearly accordant with the description of *T. Galeottiana*, which however is said to be apetalous.

**HELIOCARPUS PALMERI**. A shrub, 8 to 10 feet high, the branchlets, petioles, and inflorescence covered with a very short substellate tomentum: leaves thinly stellate-pubescent beneath, stellate-puberulent above, round-ovate to broadly lanceolate, acuminate, cordate or truncate at base, unequally and bluntly serrate, 3 to 6 inches long by 2 to 4 inches broad, on petioles 1 or 2 inches long: panicle leafy, diffuse, 4 to 6 inches long, the peduncles and pedicels very short: sepals 5, appendaged near the apex, densely puberulent, about 2 lines long: stamens 20: fruit densely stellate-pubescent, with a dense fringe of plumose hairs, less than a line broad. — Hacienda San Miguel (97, 191).

**HELIOCARPUS ATTENUATUS**. A shrub, 8 feet high, the branches and petioles softly pubescent: leaves stellate-pubescent beneath, the pubescence above somewhat thinner and shorter, ovate-lanceolate, narrowly attenuate above, cordate or rounded at base, bluntly serrate, occasionally slightly 3-lobed, 2 to 4 inches long by  $\frac{3}{4}$  to  $1\frac{1}{2}$  wide: panicle short, diffuse, with short lax branches, the slender peduncles and pedicels 2 to 4 lines long: flowers greenish yellow; calyx finely tomentose, 2 or  $2\frac{1}{2}$  lines long, the 4 or 5 sepals appendaged; petals linear, less than a line long: stamens 16: style 2-cleft; fruit pale pink, rugose and tomentose, the fringe  $1\frac{1}{2}$  lines broad. — Same locality (99).

**HELIOCARPUS POLYANDRUS**. A diffusely spreading bush, 10 feet high; branches and petioles very finely puberulent: leaves thin, nearly glabrous, somewhat scabrous on the veins, ovate, narrowly acuminate, cordate at base, obtusely serrate, 3 to 5 inches long by 2 or 3 broad, on slender petioles 1 or 2 inches long: panicle naked, rough-puberulent, diffuse with straight spreading branches; peduncles and pedicels short: sepals 5, appendaged, 2 lines long; petals a little shorter, yellow, linear: stamens about 40: fruit unknown. — Same locality (100).

**GALPHIMIA VESTITA.** Densely villous-pubescent throughout: stems numerous from a perennial caudex, a span high, branching above: leaves narrowly lanceolate, acuminate, nearly sessile, glandular near the base, 1 to  $1\frac{1}{2}$  inches long; stipules free, linear: racemes short, the bracts equalling the pedicels (2 or 3 lines long): calyx-lobes  $2\frac{1}{2}$  lines long: styles elongated, exerted; ovary glabrous. — Same locality (187).

**GAUDICHAUDIA PALMERI.** Young stems appressed-silky: leaves appressed-silky beneath, nearly glabrous above, oblong or the larger oblong-ovate, abruptly acute, rounded at base, 1 or 2 inches long, on very short petioles: normal flowers upon a short 3-flowered bibracteate peduncle, the slender pedicels 4 to 6 lines long; the 2 or 3 sterile filaments nearly equalling the others, slender, the apex subulate; abnormal fertile flowers nearly sessile in the axils: samara with a lateral wing nerved on the inner side, the dorsal and lower wings short and narrow. — Same locality (132).

**TRIBULUS GRANDIFLORUS**, Benth. & Hook. — Same locality (108).

**GERANIUM MEXICANUM**, HBK. — Yerba Buena (305).

**GERANIUM WISLIZENI.** Resembling the last, but the leaves more obtusely lobed, the pedicels soon divaricate and geniculate, and the carpels beaked with a longer style. — Norogachi, in clefts of rocks (428); also collected by Dr. Wislizenus on the Llanos mountains, Chihuahua, and referred by Dr. Engelmann (Pl. Fendler, 27) to *G. Hernandezii*, and by myself (Proc. Amer. Acad. 17. 334) to *G. Mexicanum*.

**GERANIUM NIVEUM.** Perennial, the stems a foot high or more, appressed-strigose: leaves mostly radical, white with a closely appressed silky pubescence, circular in outline, 5-7-divided, the divisions deeply 3-5-cleft into linear segments: pedicels elongated, divaricate, with short spreading glandular pubescence: sepals silky-pubescent and somewhat villous, 4 or 5 lines long: beaks of the carpels 8 or 9 lines long, hispid; style cleft nearly to the base. — Norogachi, in moist grassy openings (406).

**ERODIUM CICUTARIUM**, Linn. — Same locality (394).

**PTELEA ANGUSTIFOLIA**, Benth. A shrub, 8 or 10 feet high. — Hacienda San Miguel (152).

**BURSERA GRAVEOLENS**, Trien. & Planch. A "copal-varnish tree," about 15 feet high and 18 inches in diameter, with a few stiff branches: wood with large pith and exceedingly brittle: leaflets 3 to 6 pairs. — Same locality (Y).

**BURSERA BIPINNATA**, Engler. A "copal-varnish tree," 10 feet high and 2 to 6 inches in diameter, with short compact branches and

very brittle wood: nut black toward the summit and covered below by a fleshy orange-colored pulp. — Same locality (200). Known as "Jaboncillo."

*BURSERA FRAGILIS*. A "copal-varnish tree," 10 or 12 feet high by 2 or 3 inches in diameter, extremely brittle: leaves clustered at the ends of the branchlets, glabrous, pinnate; leaflets 1 or 2 pairs, lanceolate, acuminate, cuneate at base, finely crenate-serrate, 1 to 2½ inches long, the slender petiole channelled above and the rhachis narrowly winged: peduncles axillary, 1-2-flowered, 3 to 6 lines long: fruit obovate, obtusely triangular, 3-valved, 3 to 5 lines long; nut covered with a thin yellowish fleshy coat. — Same locality (W). Known as "Tosote."

*ILEX (AQUIFOLIUM) RUBRA*. A small tree, 15 or 20 feet high and a foot in diameter: leaves dark green and coriaceous, glabrous beneath and with very fine scattered pubescence above, oblong-ob lanceolate, acute, subattenuate at base into a short petiole (4 lines long), sparingly and acutely serrulate toward the top, 1½ to 2 inches long: fruit solitary in the axils, red, globose, nearly 4 lines in diameter, equalling the puberulent pedicel; nutlets 4, longitudinally grooved on the back and sides. — Norogachi, on stream-banks (322).

*WIMMERIA CONFUSA*, Hemsl. A shrub, 10 to 15 feet high and 3 inches in diameter, "with the habit of a plum tree": leaves narrowly oblong or oblong-lanceolate or subspatulate, attenuate to a slender petiole, crenate, ½ to 2 inches long: flowers white, 3 or 4 lines broad, on slender pedicels (3 lines long) rather exceeding the peduncle: fruit broadly winged, somewhat broader than high, 4 lines long, emarginate at both ends, tipped with a slender style nearly a line long, 1-seeded. — Hacienda San Miguel (120) and Frayles (261, 262). The fruit is much smaller and the leaves narrower in proportion than in *W. concolor*.

*KARWINSKIA HUMBOLDTIANA*, Zucc. — Hacienda San Miguel (N). "Cacachila." A decoction of the leaves is used as a remedy in fevers.

*CEANOTHUS BUXIFOLIUS*, Willd. Flowers white tinged with purple, but slightly exserted beyond the bud-scales. — At Cumbre (320).

*COLUBRINA GLOMERATA*, Hemsl.? A shrub, 4 feet high: leaves small (1 or 2 inches long), narrowly acuminate: flowers few (3 or 4) in the clusters. — Hacienda San Miguel (112).

*GOUANIA DOMINGENSIS*, Linn.? Trailing, along water-courses; apparently identical in flowers, foliage, and pubescence with West Indian specimens. There are, however, broad conspicuous stipules on the main stem, and the body of the reticulated fruit (5 lines broad) is

as broad as the rather thin wings; seed larger ( $1\frac{2}{3}$  lines long). — Same locality (18).

*VITIS ARIZONICA*, Engelm. Trailing over rocks and bushes: fruit black and sweet. — Norogachi (TT).

*CARDIOSPERMUM MOLLE*, HBK. — Hacienda San Miguel (106).

*SAPINDUS SAPONARIA*, Linn.? A small tree, 15 to 20 feet high and 2 feet in diameter: leaflet 2 to 5 pairs, narrowly oblong-lanceolate, acuminate, cuneate at base, finely pubescent beneath, especially on the nerves, as well as the narrowly winged rhachis, very variable in size (1 to 6 inches long): inflorescence finely pubescent: fruit often in threes. — Same locality (G); called "Monnie." The same as 1466 Bourgeau, from the valley of Cordova.

*DODONÆA VISCOSA*, Linn. A shrub, 5 to 10 feet high. — Hacienda San Miguel (143) and Frayles (287).

*ALVARADOA AMORPHOIDES*, Liebm. A shrub or small tree, 8 or 10 feet high and sometimes a foot in diameter. — Hacienda San Miguel (186, 240, 243).

*CROTALARIA INCANA*, Linn. — Same locality (109).

*CROTALARIA PUMILA*, Ort. — Same locality (146).

*LUPINUS CHIHUAHUENSIS*. Annual, erect and branching, finely roughish pubescent and somewhat villous: stipules conspicuous, linear with long filiform apex; petioles long; leaflets 5 or 6, oblanceolate, acute, thinly villous and ciliate: flowers in elongated pedunculate scabrous racemes, verticillate, with linear mostly deciduous bracts; pedicels very short: calyx appressed-pubescent,  $2\frac{1}{2}$  lines long; petals blue, broad, twice longer: pod villous, 6-seeded, an inch long or less. — At Cumbre (318).

*TRIFOLIUM INVOLUCRATUM*, Willd. — Yerba Buena (309).

*TRIFOLIUM AMABILE*, HBK. A form with oblong-obovate or oblanceolate leaves, obtuse or acute. — Norogachi (383).

*HOSACKIA PUBERULA*, Benth. — Same locality (433).

*EYSENHARDTIA ORTHOCARPA*, Watson. A bush, 8 or 10 feet high. — Frayles (289).

*DALEA FILIFORMIS*, Gray. — Norogachi (400).

*DALEA WISLIZENI*, Gray. — Same locality (378).

*DALEA LEUCOSTACHYS*, Gray. A shrub, 8 feet high, with white flowers. — San Jose (26); previously collected only by Wislizenus.

*DALEA NUTANS*, Willd. A shrub, 6 feet high. — Yerba Buena (298).

*DALEA PRINGLEI*, Gray. The spikes loose and much elongated. — Hacienda San Miguel (241).

*DALEA LÆVIGATA*, Gray? Perhaps an annual form; flowers white. — Frayles (254).

*DALEA* —? A low herbaceous somewhat villous perennial, with short leaves (leaflets small, 4 to 9 pairs), short dense spikes of white flowers, small deciduous bracts, and attenuate calyx-teeth as long as the tube. — Frayles (252).

*DALEA* —? A glabrous annual; leaflets 6 to 10 pairs (3 lines long): spikes dense, short, with narrow deciduous bracts: calyx-teeth lax and slender, as long as the tube and equalling the small petals: pod thin and scarious except along the upper margin. — On sandbars, Norogachi (427).

*INDIGOFERA ANIL*, Linn. — Hacienda San Miguel (80). "Añil"; used as a dye.

*TEPHROSIA TENELLA*, Gray. — Same locality (214).

*TEPHROSIA AFFINIS*. Near *T. onobrychoides*, woody at base, erect, branching, very finely appressed-pubescent: leaflets 4 to 6 pairs, oblong, obtuse or usually emarginate at the summit, narrowed below to a short petiolule, glabrous above, appressed-pubescent beneath, 1 to 1½ inches long: racemes loose, axillary, exceeding the leaves, the terminal branched; flowers rose-colored, 6 or 8 lines long, the short pedicels and calyx with a fine appressed pubescence: young pod glabrous. — Hacienda San Jose (55).

*COURSETIA* (?) *MEXICANA*. A small tree, with unequally pinnate leaves; leaflets 5 pairs, oblong-elliptical, obtuse at each end or sub-emarginate, somewhat inequilateral, an inch long or less by 6 lines wide, finely and softly pubescent, especially beneath: racemes axillary, loosely flowered, equalling or shorter than the leaves: calyx narrow, persistent: pod thin, flat, narrowed at each end, puberulent, dehiscent, 2 to 4 inches long and 4 lines wide: seeds broad-reniform (5 lines long), smooth and shining, pale salmon-color. — Hacienda San Miguel (C). "Palo piojo" or "nesco."

*NISSOLIA SCHOTTII*, Gray. Haciendas San Jose (57) and San Miguel (113).

*NISSOLIA CONFERTIFLORA*. Finely pubescent: leaflets 5, oblong-ovate, acute, rounded at base, 8 to 20 lines long: flowers small (2 lines long) in dense axillary fascicles, on pedicels 1 or 2 lines long; calyx campanulate, less than a line long: ovary densely pubescent, about 4-ovuled. — Hacienda San Jose (42).

*ÆSCHYNOMENE FASCICULARIS*, Schlecht. & Cham. A well-marked species of the section *Ochopodium*, with 10 to 20 pairs of oblong leaflets (4 or 5 lines long), sulphur-colored flowers in axillary fascicles,

and deeply parted 4-jointed pods, the joints 4 lines long. — Hacienda San Miguel (178).

*DESMODIUM (CHALARIUM) BIOCULATUM*. Herbaceous, erect, canescent with dense soft spreading pubescence: stipules lanceolate, erect; leaves 3-foliolate, with filiform persistent stipels; leaflets elliptical, rounded or subacute at both ends, covered with very soft dense appressed pubescence, greener above, the veins beneath whiter, 1 or 2 inches long by 7 to 14 lines wide, on stout petiolules: racemes axillary and terminal, simple, elongated; bracts very small; pedicels fascicled, slender, 3 lines long: calyx villous,  $1\frac{1}{2}$  lines long; petals purple, the banner with two green spots at base, 4 lines long: pod densely pubescent, nearly equally notched on both margins, the stipe twice longer than the calyx; joints (1-4) elliptical, 3 lines long. — Same locality (168).

*VICIA MEDIOCINCTA*. Low, branching from the base, sparsely villous: stipules linear; leaflets 2 or 4, very narrowly linear, 4 to 10 lines long, acuminate: flowers solitary on pedicels 3 to 6 lines long: calyx somewhat pubescent, 2 lines long, the slender teeth about equaling the tube; petals white or ochroleucous, 4 lines long: style densely bearded in the middle; pod appressed-pubescent, linear, attenuate at each end, about 10-seeded, an inch long. — Cumbre (341).

*ERYTHRINA CORALLOIDES*, DC. A small tree, closely covered with short stiff thorns: seeds large (8 lines long and 5 in diameter). — Hacienda San Miguel (E). "Chilicote" or "Pionillo"; seeds used as an emetic.

*GALACTIA TENUIFLORA*, Wight & Arn. Apparently a soft-pubescent form of this variable species. — Same locality (165).

*GALACTIA*, sp.? A small prostrate species, with nearly sessile small round-obovate leaflets and oblong 3-nerved stipules; flowers few, axillary; calyx tubular, 4-toothed; pod densely hairy, 8-10-seeded,  $\frac{3}{4}$  inch long. — Norogachi (422).

*PHASEOLUS BILOBATUS*, Engelm. — Hacienda San Jose (33).

*CÆSALPINIA PULCHERRIMA*, Swartz. — Along water-courses, same locality (B). Green seeds eaten raw, having the taste of green peas.

*CÆSALPINIA (?) PLATYLOBA*. A small tree, 12 feet high and 6 inches in diameter, very finely pubescent, the young shoots and leaves densely rufous-tomentose: pinnae 3 pairs, upon a common petiole 4 to 6 inches long; leaflets 5 or 6 pairs (rhachis 4 to 6 inches), elliptical, oblique at base, rounded at both ends, 1 or 2 inches long, sparsely pubescent: raceme terminal upon a short branch, shorter than the leaves; fruiting pedicels 6 or 8 lines long, jointed toward the top:

pod flat, thin-coriaceous, indehiscent, glabrate, 3 inches long by  $1\frac{1}{4}$  broad, obtuse, apiculate, abruptly narrowed at base to a short stipe (a line long) or rounded and sessile, not septate, 3-5-seeded: seeds flat, elliptical, 5 lines long. — On rocky mountain-sides at Hacienda San Miguel (K), called "Palo colorado," and the wood used for making bows and hoops. Very similar to an undetermined species (ticketed by Mr. Benthams "*Cæsalpinia* aff.") collected by Fendler (n. 1864) near Tovar in Venezuela, which is more coarsely pubescent, the single leaf (in herb. Gray) with two pairs of pinnæ and oblong- or ovate-lanceolate acute leaflets, and the pubescent pods (5 by  $1\frac{1}{2}$  inches) upon a stipe 5 or 6 lines long.

**HÆMATOXYLON BOREALE.** A shrub or small tree, 8 to 12 feet high and 6 inches in diameter, armed with stout axillary thorns (3 or 4 lines long): leaves glabrous, simply pinnate with 3 pairs of leaflets or the lowest pair developed into pinnæ of 1 or 2 pairs; leaflets round-ovate, mostly emarginate, finely pinnate-veined, 6 lines long or less: racemes short, simple and sessile in the axils or terminal and paniced, the slender pedicels  $\frac{1}{2}$  inch long or less: calyx-disk 2 lines broad; petals yellow, round-ovate (4 lines long): ovary and filiform style pubescent; pod 1 to  $1\frac{1}{2}$  inches long. — Closely resembling *H. Campecheanum* in foliage, but the larger flowers in shorter and more open racemes, with a much broader calyx and broader petals. Known as "Brazil," and the wood used as a red dye. Hacienda San Miguel (247, T).

**CASSIA LEPTOCARPA**, Benth. — Same locality (167).

**CASSIA OCCIDENTALIS**, Linn. — Same locality (190).

**CASSIA BIFLORA**, Linn. ? Leaflets 3 to 6 pairs; pod falcate, 3 or 4 inches long. — Hacienda San Jose (72).

**CASSIA EMARGINATA**, Linn. A small tree, 15 feet high and a foot in diameter, with a very offensive odor: leaflets 2 pairs, 2 to 4 inches long: pod 15 inches long. — Hacienda San Miguel (210); collected also by Berlandier between Tula and Tampico.

**CASSIA NICTITANS**, Linn., var., with unusually long pedicels (3 or 4 lines) and the glands of the petioles raised upon a slender stipe. — Same locality (175).

**DESMANTHUS BICORNUTUS.** Near *D. leptolobus*: herbaceous, erect, 4 feet high, glabrous: leaves with long filiform stipules, and a conspicuous bifid gland near the base of the petioles; pinnæ 10 to 13 pairs, the numerous acute leaflets a line long: peduncles axillary and in a terminal leafy raceme, the lower shorter than the leaves: pod straight, narrowly linear, 1 or 2 inches long, 10-15-seeded. — San Jose (43).

*MIMOSA LAXIFLORA*, Benth.? A shrub, 8 feet high, with stout scattered recurved prickles or the slender branches sometimes unarmed, glabrous: pinnæ 2 or 3 pairs; leaflets 2 to 4 pairs, oblong to broadly elliptical or semicordate, 2 to 4 lines long: flowers pentamerous, pedicellate, in short loose shortly pedunculate spikes; stamens 10: pod unarmed, thin, about 20 lines long by 3 broad. — Differing slightly from the description of the original of the species collected by Coulter in northern Sonora. As suggested by Bentham, it is probably the same as *Acacia prosopoides*, DC. Same locality (41); found also by Pringle in 1884 in the mountains of northwestern Sonora.

*LEUCÆNA LANCEOLATA*. Resembling *L. retusa*: a shrub, 5 feet high, finely pubescent: leaves with a prominent gland above the base of the long petioles; pinnæ 2 or 3 pairs; leaflets 6 or 7 pairs, lanceolate, very acute, finely pubescent,  $\frac{1}{2}$  to 1 inch long, a small gland below the upper pair: peduncles  $1\frac{1}{2}$  inches long: flowers white, in large heads. — Hacienda San Miguel (6). *L. retusa* is more glabrous, the leaflets mostly obtuse or retuse, the shorter petiole with a gland between the lower pinnæ, and the pinnæ glanduliferous between each pair of leaflets.

*ACACIA MILLEFOLIA*. A shrub or small tree, 10 feet high, with slender branches and armed with slender ascending stipular prickles (1 or 2 lines long), sparingly pubescent: rhachis of the leaves sulcate: pinnæ 5 to 10 pairs, about an inch long; leaflets 25 to 35 pairs, linear, acute, 1 or  $1\frac{1}{2}$  lines long: peduncles axillary, bearing loose spikes (1 or  $1\frac{1}{2}$  inches long) of white or pale yellow flowers: pod chartaceous, thin and flat, somewhat curved, 3 to 5 inches long and 9 lines wide, 5-10-seeded, stipitate: seed round, flat, 3 or 4 lines broad. — Hacienda San Jose (45); first discovered by C. G. Pringle in July, 1884, in flower only, on the foot-hills of the Santa Rita Mountains, Arizona. Nearest to *A. Emoryi*.

*ACACIA COCHLIACANTHA*, Humb. & Bonpl. A small tree, 10 feet high, with stout cochleate spines ( $\frac{1}{2}$  to nearly 2 inches long), and fragrant orange-colored flowers in small globose heads: pods glabrous, thin-coriaceous, indehiscent (?), flattened, falcate, 3 inches long by 4 lines broad, stipitate, about 12-seeded. — Hacienda San Miguel (71).

*CALLIANDRA GRANDIFLORA*, Benth. — Hacienda San Jose (36) and Frayles (266).

*CALLIANDRA RETICULATA*, Gray. — Norogachi (370).

*CALLIANDRA COULTERI*, Watson. — Pods glabrous, 3 inches long and 3 lines wide, the valves thin. — Hacienda San Miguel, in flower, and later in fruit (16, 223). These fruiting and flowering specimens

appear to belong to the same species, though the leaflets of the former are mostly larger (2 to 7 lines long and 1 to 4 wide) and very variable in form.

*PITHECOLOBIUM DULCE*, Benth. A tree, 25 or 30 feet high and 3 to 5 feet in diameter, with very hard and durable wood, fruiting abundantly; pods 6 inches long, the black seeds (5 lines long) imbedded in the white spongy edible aril. — Hacienda San Miguel (D).

*FRAGARIA MEXICANA*, Schlecht. — Yerba Buena (313).

*POTENTILLA THURBERI*, Gray. — Norogachi (426).

*ALCHEMILLA SIBBALDIEFOLIA*, HBK. — Yerba Buena (304).

*SEDUM* —? Too imperfect for determination. — Norogachi (373).

*SEDUM VINICOLOR*. Annual, low (3 inches), the stout stem diffusely much-branched, glabrous: upper leaves imbricated, oblong-ovate, somewhat concave, 2 or 3 lines long, "of a dark wine-color": flowers in clusters of 2 to 5 at the ends of the branchlets, very shortly pedicellate: sepals purple, distinct, oblong-ovate, somewhat cucullate at the apex, unequal, about a line long; petals twice longer, greenish white, narrowly oblong, obtuse: stamens 10; scales at the base of the carpels purple, oblong-obovate: carpels purple, divergent, equalling the petals. — In the crevices of rocks; Norogachi (374).

*SEDUM FILIFERUM*. Perennial, caespitose, glabrous, the branching rootstock bearing rosettes of numerous spatulate leaves, 4 to 8 lines long, which are abruptly acute and attenuate into filiform appendages or setae 2 or 3 lines long: flowering stem lateral, slender, naked, ascending, about 4 inches high, bearing an open cyme; pedicels 3 or 4 lines long: sepals oblong (2 lines long), pointed with a short seta; petals spreading, narrowly lanceolate, acute, nearly twice longer than the sepals, white below, reddish above: stamens 10, exceeding the sepals and oblong carpels. — Raised in Washington from seeds collected by Dr. Palmer in Chihuahua.

*CUPHEA LLAVEA*, Llav. & Lex. — Hacienda San Jose (28).

*CUPHEA PALMERI*. Annual; stem erect, viscid-pubescent, 1 to 1½ feet high: leaves ovate-lanceolate, acute, cuneate or usually rounded at base, scabrous, 1 or 2 inches long, the glandular-pubescent petiole 2 to 6 lines long, reduced above to linear hirsute bracts: flowers 1 to 3 in the axils, on pedicels 2 lines long or less. calyx 5 lines long, narrow in flower, gibbous, hirsute on the veins, the dorsal lobe produced; petals purple, the dorsal 3 lines long, with a rounded blade, the others linear-spatulate, about equalling the claws of the dorsal; stamens nearly equal and glabrous or more or less bearded, the dorsal pair shorter and villous: disk round, thick, ascending: seeds 3, narrowly margined.

— Nearly related to *C. Wrightii* and *C. viscosissima*. Hacienda San Miguel (127).

**LOPEZIA CORNUTA.** Annual, low, slender, glabrous or sparingly villous: lower leaves opposite, the rest alternate, petiolate, oblong to linear-lanceolate, acute or acuminate, mostly cuneate at base, entire or obscurely sinuate, the larger an inch long: pedicels spreading or reflexed: petals purple, the lower orbicular, equalling the narrowly oblong upper ones; sterile stamen round-obcordate or reniform, as long as the lower petals, white: capsule obovate, opening at the summit, obtusely 4-beaked between the valves. — Cumbre (367). Remarkable for its beaked capsule.

**LOPEZIA GRACILIS.** Annual, low, glabrous, very slender: lower leaves opposite, the upper alternate, linear-oblong, obtuse, attenuate to the base, entire: pedicels ascending: petals purple, the lower obovate, shorter than the oblong upper ones, nearly twice longer than the white obcordate sterile stamen: capsule quadrangular-obovate, dehiscing to the middle. — Same locality (337).

**GONGYLOCARPUS RUBRICAULIS**, Cham. & Schlecht. — Hacienda San Jose (34).

**GRONOVIA SCANDENS**, Linn. — Frayles (293).

**MENTZELIA ASPERA**, Linn. — Hacienda San Miguel (101).

**PASSIFLORA FETIDA**, Linn. — Same locality (199).

**PASSIFLORA INAMENA**, Gray. — Hacienda San Jose (32).

**CUCURBITA FETIDISSIMA**, HBK.? Leaves much more obtuse than in the ordinary form. — Norogachi (NN); "Chili coyote."

**SICYOSPERMA GRACILE**, Gray. — Hacienda San Miguel (148).

**MICROSECHIMUM RUDERALE**, Naud. — Norogachi (396).

**BEGONIA PALMERI.** Stem herbaceous from a tuberous rootstock, glandular-pubescent: leaves obliquely cordate, palmately 5-nerved, subacuminate, the broader side somewhat 2-3-lobed, acutely toothed and denticulate, sparsely pubescent; petioles glandular-pubescent: inflorescence glabrous; male flowers 2-sepalled, 2-petalled; stamens numerous, the slender filaments covering the elongated staminal column and exceeding the broadly elliptical anthers; fertile flowers with 3 unequal lobes: styles persistent, very short, twice 2-parted, the segments stigmatose at the curved summit: capsule unequally 3-winged, subquadrate in outline but broader above; placenta 2-parted. — Hacienda San Miguel (139). Not referable satisfactorily to any of the numerous sections proposed by A. DeCandolle.

**CEREUS (LEPIDOCEREUS) PECTEN-ABORIGINUM**, Engelm. in herb. Stems tall, erect, solitary, with few erect branches, 10-11-costate;

areolæ densely tomentose, finally glabrate; spines 8 to 12 (usually 10), very stout, straight, ash-colored tipped with black, the marginal spreading or reflexed (6 lines long or less), the central one and sometimes the two uppermost larger ( $\frac{1}{2}$  to  $1\frac{1}{2}$  inches long) and erect or ascending, compressed or angular: fruit dry, globose ( $2\frac{1}{2}$  or 3 inches in diameter), closely covered with pulvinate densely hairy areolæ, which are for the most part beset with stiff setaceous unequal yellowish spines (the longest 9 to 12 lines long): seeds large (2 lines long), black and shining; embryo hamate. — Growing 20 to 30 feet high and 2 feet in circumference, on stony mountain-sides at Hacienda San Miguel (AA); called "Cordon," or "Hecho," by the Indians, who grind the seed to mix with their meal, and use the bristly covering of the fruit as a hair-brush. The species was first made known to Dr. Engelmann by a specimen of these brushes which was obtained by Dr. Palmer in 1869 from the Papago Indians at Hermosillo in Sonora. Dr. Engelmann's notes upon his material have been found among his papers. From these it appears that the remains of the tube of the flower showed very numerous loosely imbricated linear-lanceolate sepals, 6 to 9 lines long, woolly in the axils. Palmer's present specimens, scanty, but supplemented by a photograph and by notes, are sufficient to furnish most of the needed characters and to confirm the distinctness of the species. The flowers remain unknown. *C. macrogonus*, Salm-Dyck, of unknown origin, has been in cultivation since before 1850. Plants so named in hort. Cambridge, now about three feet high, resemble the present species, and it is possible that the two species may finally prove to be the same.

*ERYNGIUM WRIGHTII*, Gray. — Norogachi (390).

*ERYNGIUM DISCOLOR*, Watson. — Same locality (397).

*ARRACACIA EDULIS*. Rather stout, glabrous, branching, a foot high or more: leaves pinnate, the upper sessile upon a dilated base; leaflets lanceolate, more or less deeply pinnatifid or pinnately parted: umbels without involucre, 10–15-rayed, the fertile rays (about 5) becoming an inch long or more; involuclers large, of several pinnatifid bracts: flowers yellow: fruit compressed-ovate, with thick corky ribs and broad vittæ filling the intervals, 3 lines long; seed involute-terete. — Same locality (HH); much used by the Indians for greens.

*DAUCUS MONTANUS*, Willd. — Yerba Buena (308).

*GARRYA OVATA*, Benth. A shrub, 8 to 12 feet high, with blue-black berries. — Cumbre (319).

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The following determinations of the Gamopetalæ of the collection were made by Dr. Gray. Descriptions of the new species and various notes by him may be found in the foregoing paper.

*GALIUM MICROPHYLLUM*, Gray. — Norogachi (413). *G. UNCINULATUM*, DC. ? — Same locality (414).

*CRUSEA SUBULATA*, Gray. — Norogachi (423). *C. PALMERI*, Gray, *n. sp.* — Hacienda San Jose (70).

*MITRACARPUS VILLOSUS*, Cham. & Schlecht. — Hacienda San Jose (38).

*SPERMACOCE MEGALOCARPA*, Gray, *n. sp.* — Hacienda San Miguel (185).

*COUTAREA LATIFLORA*, DC. — Same locality (H).

*GENIPA ECHINOCARPA*, Gray. (*Randia echinocarpa*, DC.) — Same locality (A).

*VALERIANA SORBIFOLIA*, HBK. — Norogachi (388).

*VERNONIA STEETZII*, Schultz Bip. — Frayles (273).

*STEVIA PALMERI*, Gray, *n. sp.* — Hacienda San Jose (30). *S. LINOIDES*, Schultz Bip., var. *GRISEA*, Gray. — Frayles (251). *S. LAXIFLORA*, DC. — Norogachi (418). *S. MONARDEFOLIA*, HBK., var. *CORDIFOLIA*, Gray. — Frayles (257). *S. MICRANTHA*, Lag. — Same locality (284). *S. VENOSA*, Gray, *n. sp.* — Norogachi (376). *S. SALICIFOLIA*, Cav. — Frayles (278); Norogachi (391). *S. SERRATA*, Cav. — Cumbre (338). *S. MADRENSIS*, Gray, *n. sp.* — Cumbre (328).

*CARPHOCHÆTE WISLIZENI*, Gray. — Cumbre (331).

*AGERATUM CORYMBOSUM*, Zuccag. — Haciendas San Jose (31) and San Miguel (110).

*PIPTOTHRIX PALMERI*, Gray, *n. gen.* — Frayles (274, 280).

*EUPATORIUM COLLINUM*, DC. — Frayles (271). *E. SCHAFFNERI*, Schultz Bip. — Norogachi (332). *E. STRICTUM*, Gray, *n. sp.* — Same locality (330). *E. PALMERI*, Gray, *n. sp.* — Hacienda San Miguel (144); Frayles (263). *E. GRANDIDENTATUM*, DC. — Norogachi (375). *E. VENULOSUM*, Gray, *n. sp.* — Cumbre (329). *E. OCCIDENTALE*, Hook., var. *ARIZONICUM*, Gray. — Frayles (275). *E. GUADALUPENSE*, Spreng. (*E. paniculatum*, Schrad.) — Frayles (276).

*CARMINATIA TENUIFLORA*, DC. — Hacienda San Miguel (239).

*KUHNI ROSMARINIFOLIA*, Vent. — Norogachi (437).

*BRICKELLIA SIMPLEX*, Gray. — Norogachi (436). *B. BETONICÆFOLIA*, Gray, var. *HUMILIS*, Gray. — Norogachi (435). *B. BRACHIATA*, Gray, *n. sp.* — Hacienda San Miguel (169). *B. DIFFUSA*, Gray. — Same locality (166).

- XANTHOCEPHALUM SERICOCARPUM, Gray. — Norogachi (412).
- X. GYMNOSPERMOIDES, Gray. — Norogachi (439).
- APLOPAPPUS TENULOBUS, Gray, *n. sp.* — Norogachi (408).
- SOLIDAGO BIGELOVII, Gray. — Norogachi (438).
- ACHÆTOGERON PALMERI, Gray, *n. sp.* — Cumbre (362). A. AFFINIS, Gray, *n. sp.* — Frayles (255).
- PSILACTIS ASTEROIDES, Gray. — Norogachi (410).
- ASTER EXILIS, Ell. — Hacienda San Miguel (174).
- ERIGERON NEO-MEXICANUS, Gray. — Norogachi (419). E. INOPTATUS, Gray, *n. sp.* — Norogachi (442).
- CONYZA GNAPHALOIDES, HBK. — Norogachi (404). C. SOPHLEFOLIA, HBK. — Norogachi (416).
- BACCHARIS THESIOIDES, HBK. — Hacienda San Miguel (217).
- B. MUCRONATA, HBK. — Frayles (277 male, 281 female).
- GNAPHALIUM PRINGLEI, Gray. — Norogachi (443). G. LEUCOCEPHALUM, Gray. — Norogachi (417). G. LEPTOPHYLLUM, DC. — Yerba Buena (311); Norogachi (411).
- LAGASCEA DECIPIENS, Hemsl. — Hacienda San Miguel (145).
- GUARDIOLA PLATYPHYLLA, Gray. — Hacienda San Jose (35).
- MILLERIA QUINQUEFLORA, Linn. — Hacienda San Miguel (176).
- ELVIRA BIFLORA, Cass. — Same locality (141).
- MELAMPODIUM LONGICORNU, Gray. — Frayles (245).
- PARTHENIUM TOMENTOSUM, DC. — Hacienda San Miguel (123).
- AMBROSIA PSILOSTACHYA, DC. — Norogachi (384).
- TRAGOCERAS MOCINIANUS, Gray. (*Zinnia bicuspis*, DC.) — Hacienda San Jose (67).
- ZINNIA PAUCIFLORA, Linn. — Hacienda San Miguel (115, 136).
- MONTANOA PATENS, Gray, *n. sp.* — Same locality (164).
- GYMNOLOMIA MULTIFLORA, Benth. & Hook. — Norogachi (392).
- JOSTEPHANA HETEROPHYLLA, Benth. — Cumbre (333).
- VIGUIERA HELIANTHOIDES, HBK. — Hacienda San Miguel (218).
- ENCELIA EXARISTATA, Gray. — Norogachi (440).
- ZEXMENIA FASCICULATA, Hemsl. — Hacienda San Miguel (155).
- Z. PODOCEPHALA, Gray. — Norogachi (II).
- VERBESINA PERSICÆFOLIA, DC. — Cumbre (324). V. LEPTOCHÆTA, Gray, *n. sp.* — Hacienda San Miguel (170). V. CYMOSEA, Gray, *n. sp.* — Same locality (135).
- LEPTOSYNE ARIZONICA, Gray. — Frayles (294).
- BIDENS HETEROPHYLLA, Ort. — Cumbre (365). B. ODORATA, Cav. — Frayles (283). B. LEUCANTHA, Willd. — Frayles (282).
- B. PILOSA, Linn. — Hacienda San Miguel (238). B. MOLLIS, Poepp.

& Endl.? — Norogachi (358). *B. BIPINNATA*, Linn. — Hacienda San Miguel (131). *B. PROCERA*, Don. — Cumbre (316); Norogachi (393).

*GALINSOGA PARVIFLORA*, Cav. — Frayles (286?).

*TRIDAX ERECTA*, Gray, *n. sp.* — Frayles (285). *T. BICOLOR*, Gray. — Hacienda San Miguel (130). *T. LEPTOPHYLLA*, Gray, *n. sp.* — Norogachi (425).

*PERITYLE MICROCEPHALA*, Gray. — Frayles (268).

*BAHIA NEO-MEXICANA*, Gray. — Norogachi (399).

*SCHKUHRIA WISLIZENI*, Gray. — Norogachi (387).

*HYMENOTHRIX PALMERI*, Gray, *n. sp.* — Norogachi (395).

*DYSODIA POROPHYLLA*, Cav. — Yerba Buena (300).

*POROPHYLLUM MACROCEPHALUM*, DC. — Hacienda San Miguel (126). *P. SEEMANNI*, Schultz Bip. — Same locality (216).

*TAGETES LUCIDA*, Cav. — Norogachi (LL). *T. MICRANTHA*, Cav. — Norogachi (GG). *T. PALMERI*, Gray, *n. sp.* — Frayles (265). *T. WISLIZENI*, Gray. — Frayles (267).

*PECTIS PROSTRATA*, Cav. — Hacienda San Jose (53). *P. BERLANDIERI*, DC., var. (?) *PALMERI*, Gray. — Same locality (61). *P. STENOPHYLLA*, Gray, *n. sp.* — Hacienda San Miguel (81).

*ARTEMISIA MEXICANA*, Willd. — Norogachi (SS).

*SENECIO HARTWEGI*, Benth. — Cumbre (366).

*CENTAUREA AMERICANA*, Nutt. — Norogachi (415).

*PEREZIA PLATYPHYLLA*, Gray. — Yerba Buena (299). *P. PANICULATA*, Gray, *n. sp.* — Frayles (279). *P. THURBERI*, Gray. — Frayles (272).

*LOBELIA SPLENDENS*, Willd. — Cumbre (368). *L. FENESTRALIS*, Cav. — Norogachi (377). *L. GRUINA*, Cav. — Norogachi (407). *L. GRACILENS*, Gray, *n. sp.* — Cumbre (360).

*ARBUTUS XALAPENSIS*, HBK. — Cumbre (321); Norogachi (VV).

*ARCTOSTAPHYLOS PUNGENS*, HBK. — Norogachi (OO).

*GAULTHERIA ODORATA*, HBK. — Cumbre (317).

*PLUMBAGO SCANDENS*, Linn. — Hacienda San Miguel (156).

*PLUMERIA MEXICANA*, Lodd. — Same locality (231).

*TABERNÆMONTANA*, *sp. allied to T. littoralis*, HBK. — Hacienda San Miguel (N), fruit only.

*PHILIBERTIA PALMERI*, Gray, *n. sp.* — Same locality (5).

*GONOLOBUS PETIOLARIS*, Gray, *n. sp.* — Same locality (7, 208).

*G. CAUDATUS*, Gray, *n. sp.* — Hacienda San Jose (75).

*BUDDLEIA HUMBOLDTIANA*, Roem. & Schult. — Cumbre (314).

*GENTIANA LANCEOLATA*, Griseb. — Cumbre (361). *G. WISLIZENI*, Engelm. — Cumbre (334). *G. WRIGHTII*, Gray. — Yerba Buena (306). *G. ADSURGENS*, Cerv. — Cumbre (335).

*HALENIA PARVIFLORA*, Don, var. *LATIFOLIA*, Griseb. — Norogachi (403). *H. PALMERI*, Gray, *n. sp.* — Cumbre (359).

*GILIA FLORIBUNDA*, Gray. — Norogachi (398). *G. PRINGLEI*, Gray. — Norogachi (431).

*LCESELIA COCCINEA*, Don. — Frayles (253). *L. CÆRULEA*, Don. — Frayles (256). *L. CILIATA*, Linn. — Hacienda San Miguel (193).

*BONPLANDIA GEMINIFLORA*, Cav. — Same locality (232).

*PHACELIA CIRGINATA*, Jacq. — Norogachi (389).

*HELIOTROPIMUM INDICUM*, Linn. — Hacienda San Jose (44). *H. FRUTICOSUM*, Linn. — Hacienda San Miguel (13, 98).

*LITHOSPERMUM MULTIFLORUM*, Torr. — Norogachi (386).

*IPOMŒA COCCINEA*, Linn., var. *hederifolia*, Gray. — Hacienda San Miguel (103). *I. RUBROCÆRULEA*, Hook. — Same locality (102).

*I. COSTELLATA*, Torr. — Same locality (104). *I. HEDERACEA*, Jacq.

— Same locality (105). *I. TRILOBA*, Linn. — Same locality (213).

*I. BONA-NOX*, Linn. — Same locality (244). *I.* — ?, with thick

edible roots. — Same locality (R). *I. BRACTEATA*, Cav. — Frayles

(296). *I. LONGIFOLIA*, Benth. — Frayles (297).

*JACQUEMONTIA PRINGLEI*, Gray, var. *GLABRESCENS*, Gray. — Hacienda San Miguel (107, 248).

*EVOLVULUS ALSINOIDES*, Linn. — Hacienda San Miguel (183).

*CUSCUTA TINCTORIA*, Engelm. — Same locality (142, 227).

*SOLANUM VERBASCÆFOLIUM*, Linn. — Hacienda San Miguel (11).

*S. DIVERSIFOLIUM*, Schlecht., fide Hemsley. — Same locality (22). *S.*

*NIGRUM*, Linn., var. — Same locality (204). *S. ELÆAGNIFOLIUM*,

Cav. — Same locality (237). *S. SISYMBRIIFOLIUM*, Lam. — Hacienda

San Jose (54).

*CAPSICUM BACCATUM*, Linn. — Hacienda San Miguel (230).

*PHYSALIS ÆQUATA*, Jacq. f. ? — Same locality (140). *P. NICANDROIDES*, Schlecht. ? — Same locality (226).

*DATURA METELOIDES*, DC. — Same locality (Z<sup>1</sup>). *D. ALBA*, Nees ? — Same locality (Z<sup>2</sup>).

*NICOTIANA RUSTICA*, Linn. — Norogachi (RR). *N. TRIGONOPHYLLA*, Dunal. — Hacienda San Miguel (114).

*RUSSELLIA SARMENTOSA*, Jacq. — Same locality (249).

*PENTSTEMON COCCINEUS*, Engelm., var. *FILIFOLIUS*, Gray. — Norogachi (432). *P. FASCICULATUS*, Gray, *n. sp.* — Frayles (264).

*P. CAMPANULATUS*, Willd. — Yerba Buena (307).

- MIMULUS GLABRATUS, HBK., var. JAMESII, Gray. — Hacienda San Jose (62).
- CONOBEA INTERMEDIA, Gray. — Hacienda San Miguel (188).
- STEMODIA PALMERI, Gray, *n. sp.* — Same locality (221, 250). S.
- DURANTIFOLIA, Swartz. — Hacienda San Jose (74).
- SEYMERIA BIPINNATISECTA, Seem. — Cumbre (325).
- LAMOUREUXIA CORDATA, Cham. & Schlecht. — Frayles (258).
- L. HYSSOPIFOLIA, Gray, *n. sp.* — Frayles (260).
- CASTILLEIA TENUIFLORA, Benth. — Cumbre (363).
- PEDICULARIS ANGUSTIFOLIA, Benth. — Cumbre (326).
- TECOMA STANS, Juss. — Hacienda San Miguel (151).
- MARTYNIA FRAGRANS, Lindl. — Same locality (192).
- ELYTRARIA TRIDENTATA, Vahl. — Norogachi (EE).
- CALOPHANES BILABIATA, Seem. — Hacienda San Miguel (235).
- JACOBINIA OVATA, Gray, *n. sp.* — Same locality (220).
- JUSTICIA CAUDATA, Gray, *n. sp.* — Same locality (189).
- CARLOWRIGHTIA CORDIFOLIA, Gray, *n. sp.* — Same locality (224).
- TETRAMERIUM HISPIDUM, Nees. — Same locality (125).
- HENRYA COSTATA, Gray, *n. sp.* — Same locality (211).
- LANTANA VELUTINA, Mart. & Gal.? — Same locality (15).
- LIPPIA PURPUREA, Jacq. f. — Same locality (129).
- VERBENA POLYSTACHYA, HBK. — Norogachi (364). V. CILIATA, Benth. — Frayles (295).
- VITEX MOLLIS, HBK. — Hacienda San Miguel (U).
- OCIMUM MICRANTHUM, Willd.? — Frayles (290).
- HYPTIS SPICATA, Poit. — Hacienda San Miguel (124). H. SEEMANNI, Gray, *n. sp.* — Same locality (177). H. ALBIDA, HBK. — Same locality (198).
- MENTHA CANADENSIS, Linn. — Norogachi (429).
- HEDEOMA COSTATA, Gray. — Norogachi (441).
- MONARDA CITRIODORA, Cerv. — Norogachi (401).
- SALVIA TILLEFOLIA, Vahl. — Norogachi (MM). S. PRIVOIDES, Benth. — Hacienda San Jose (64). S. ALBIFLORA, Mart. & Gal.? — Hacienda San Miguel (154), and a cærulescent form (96, 157). S. HYPTOIDES, Mart. & Gal. — Same locality (205). S. ELEGANS, Vahl. — Same locality (270). S. SCORDONIEFOLIA, Poir. — Same locality (O). S. PALMERI, Gray, *n. sp.* — Frayles (259). S. COCCINEA, Jacq. — Cumbre (315). S. MICROPHYLLA, HBK., var. WISLIZENI, Gray. — Norogachi (379).
- CEDRONELLA CANA, Hook. — Norogachi (FF). C. MICRANTHA, Gray, and C. AURANTIACA, Gray, *n. sp.* — Norogachi (420, and 402).

*BRUNELLA VULGARIS*, Linn. — Cumbre (327).

*PLANTAGO HIRTELLA*, HBK. — Yerba Buena (311). *P. PATAGONICA*, Jacq. — Same locality (312).

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*OXYBAPHUS CERVANTESII*, Sweet; the more viscid-pubescent form. — Hacienda San Miguel (233).

*BOERHAAVIA PANICULATA*, Rich. Flowers dark red. — Same locality (202).

*BOERHAAVIA SPICATA*, Choisy, var. With flowering racemes very short (2 or 3 lines) and dense (about 25-flowered), the pinkish flowers a line long; fruiting racemes also shorter and more crowded, the fruit only a line long. — Same locality (209).

*BOERHAAVIA VISCOSA*, Lag. & Rodr. Flowers dark red. — Same locality (212).

*BOERHAAVIA ERECTA*, Linn. — Same locality (225).

*AMARANTUS PALMERI*, Watson. Staminate; often 8 feet high. — Hacienda San Miguel (V). Young stems and leaves eaten for greens.

*AMARANTUS (AMBLOGYNE) CHIHUAHUENSIS*. Monœcious; erect, sparingly pubescent, 1 or 2 feet high: leaves ovate-lanceolate to oblong, obtusish, narrowed at base, an inch or two long including the slender petiole, the floral much reduced: flowers clustered in all the axils and in long slender terminal more or less naked spikes; bracts solitary, small and narrow: staminate flowers mingled with the pistillate; sepals scarious, oblong, acute, those of the urceolate fertile flowers broadly spatulate, entire, setose-apiculate, the green midvein somewhat branched, becoming much thickened at base, less than a line long: utricle smooth: seed brown, shining. — With unusually small flowers for the section, and rather peculiar in habit. Hacienda San Miguel (197).

*GUILLEMINEA ILLECEBROIDES*, HBK. — Norogachi (382).

*TELANTHERA (BUCHOLTZIA) STELLATA*. Annual, ascending, loosely branched, 2 feet high, roughish throughout with short stellate pubescence: leaves ovate to lanceolate, acute, narrowed to a short petiole, less pubescent above, 1 to  $1\frac{1}{2}$  inches long: heads small, solitary or few in the axils; bracts lanceolate, glabrous, shorter than the dorsally compressed perianth: outer perianth-segments 3-nerved, rigid, pubescent with simple hairs, acuminate, 2 lines long: staminodia narrow, lanceolate, exceeding the stamens. — Hacienda San Miguel (4), among underbrush.

*ALTERNANTHERA ACHYRANTHA*, R. Br. — Norogachi (405).

*GOMPHRENA DECIPIENS*. Erect, branched, 2 feet high, sparingly pilose, more densely so at the nodes and on the young branches: leaves oblong-lanceolate or oblanceolate, acute or subacuminate, attenuate to a winged petiole, sparsely villous beneath,  $1\frac{1}{2}$  to 3 inches long: heads small, white, usually sessile between a pair of sessile leaves: bracts equal, without crest, hyaline, ovate, acute, very faintly nerved, 2 lines long: sepals as long, scarious, nerveless at the narrow acutish top, the nerve below green and rigid: staminal tube slightly cleft, the falcate lobes equalling the nearly sessile anthers. — Apparently distinct from *G. pilosa*, Mart. & Gal., as described in DC. Prodr. which also has the bracts crestless. Hacienda San Jose (27).

*GOMPHRENA DECUMBENS*, Jacq., var. Stems decumbent or ascending: crest of the bracts only near the summit and with 2 or 3 teeth. Like the specimens from about San Luis Potosi, collected by Schaffner and by Parry & Palmer. Specimens from other Mexican States, Central America, and Cuba, vary much in the size of the crest and slightly in the characters of the staminal tube, but appear to be essentially the same species. Hacienda San Jose (58).

*FRELICHTIA (HOPLOTHECA) ALATA*. Perennial (?); stems erect, 2 or 3 feet high, rough-pubescent: leaves oblanceolate, acute, villous-tomentose beneath, smoother above, the lower 3 or 4 inches long: spikes solitary, sessile, short (3 to 8 lines long); bracts nearly a half shorter than the calyx: calyx in fruit with broad lateral entire or slightly crenulate wings, not crested nor winged upon the back: staminal tube equalling the calyx. — Allied to the Brazilian *F. tomentosa*. Hacienda San Jose (47).

*IRESINE CELOSIODES*, Linn. — Frayles (291).

*IRESINE SCHAFFNERI*. Suffrutescent, appressed villous-pubescent, the hairs of the stem shorter and substrigose: leaves oblong-lanceolate, acute, narrowed to a slender petiole, densely whitish-silky beneath when young, becoming nearly glabrous above, very variable in size ( $\frac{1}{2}$  to 3 or 4 inches long): panicles mostly long-pedunculate, the spikes sessile and somewhat crowded upon the short branches; rachis of the spikes densely villous: flowers a line long, the staminate subpubescent and with very short bracts, the fertile with naked bracts nearly equalling the densely villous calyx. — The same as 876 Schaffner and 791 Parry & Palmer, from near San Luis Potosi. Hacienda San Miguel (12, 111).

*CHENOPodium BERLANDIERI*, Moq. — Same locality (9).

*CHENOPodium AMBROSIODES*, Linn. — Norogachi (BB); used by the Indians as a febrifuge and to flavor their food. "Iparote."

*ERIOGONUM ATRORUBENS*, Engelm. — Norogachi (JJ); known as "Yerba colorado," the large red roots much used as an astringent and for the toothache.

*ERIOGONUM POLYCLADON*, Benth. — Norogachi (385).

*POLYGONUM PERSICARIA*, Linn. — Hacienda San Miguel (137).

*ANTIGONON LEPTOPUS*, Hook. & Arn. — Hacienda San Jose (46).

*LORANTHUS (EUPSITTACANTHUS) PALMERI*. Parasitic upon *Bursera bipinnata*: stems stout: leaves opposite, broadly spatulate or obovate, rounded or truncate at the summit, attenuate to a slender petiole, glabrous, with irregularly branched veins, 1 to 1½ inches long: peduncles axillary, 3-flowered, an inch long; pedicels half as long, with a very short obliquely cupulate bract: petals 1½ inches long, "magenta-colored." — Hacienda San Miguel (219).

*EUPHORBIA DIOSCOREOIDES*, Boiss. — Same locality (134).

*EUPHORBIA PILULIFERA*, Linn. — Same locality (150).

*EUPHORBIA HETEROPHYLLA*, Linn. — Same locality (122).

*EUPHORBIA CUPHOSPERMA*, Boiss. — Same locality (95).

*EUPHORBIA ADENOPTERA*, Bertol. — Norogachi (381).

*EUPHORBIA THYMIFOLIA*, Burm. ? This species is reported to have been collected in Chihuahua by Potts, and in several other localities in Mexico and Central Mexico. Palmer's specimens appear to differ from the usual form in the more nearly sessile oblong-ovate capsule with rounded nearly nerveless lobes, and the seeds more deeply grooved. — Hacienda San Jose (77).

*EUPHORBIA SCABRELLA*, Boiss. In the more perfect involucre there are five glands; some usually remain undeveloped. — Hacienda San Miguel (121, 149).

*EUPHORBIA (CHAMÆSYCE) GRACILLIMA*. Annual, erect, very slender and diffusely branched, low, glabrous: leaves glaucous, narrowly linear with revolute entire margins, 2 to 5 lines long, on short petioles: pedicels solitary, very slender, divaricate, 1 or 2 lines long; involucre campanulate, very small (½ line long), the greenish glands with very short white appendages: capsule triangular-globose, acutely lobed, ½ line long: seed reddish, oblong, smooth, the sides somewhat concave. — Hacienda San Jose (68). Allied to *E. zygaphylloides*, Boiss.

*EUPHORBIA (ALECTOROCTONUM) PLICATA*. Suffrutescent, with long spreading branches, glabrous, 5 to 8 feet high: leaves in threes, oblong-lanceolate, obtuse or slightly emarginate or rarely acutish, cuneate at base, nearly glabrous above, finely pubescent beneath, as well as the slender petiole (4 to 6 lines long), 1 to 3 inches long, the floral linear: inflorescence very finely appressed-pubescent, the

cymes axillary and terminal, crowded, on very short peduncles; involucre campanulate, the obovate lobes lacerate at the summit; glands 5, rounded and transversely plicate, the inner fold often smaller; appendages rounded, twice larger than the gland, entire, white: capsule glabrous, 2 lines long: seed irregularly tuberculate. — Hacienda San Miguel (181, 246).

*EUPHORBIA* (*CYTTAROSPERMUM*) *SUBRENIFORME*. Annual, very slender, erect, the stem and branches glabrous, a foot high or less: leaves all opposite, on filiform petioles exceeding the thin blade, which is subreniform, rounded-truncate and slightly apiculate or emarginate at summit, shortly cuneate at base, sparingly villous and ciliate, the largest 6 lines broad: involucre solitary, very small ( $\frac{1}{4}$  line long), villous; lobes entire or nearly so, ciliate; glands 4, purple, stipitate, rounded, with an appendage of 3 or 4 long purple setæ: styles purple, 2-parted; capsule villous,  $\frac{3}{4}$  line long: seeds oblong-ovate, the shallow pits tuberculate-margined and punctate in the centre. — Hacienda San Jose (60), and Frayles (292).

*JATROPHA CORDATA*, Muell. Arg. — Norogachi (CC); known as "Matamuchachos." The bruised leaves are applied to sores, and added to the water in which children are bathed, to impart vigor.

*CROTON FRAGILIS*, Muell. Arg., var. *SERICEUS*, Muell. Arg.? Fruiting specimens, shrubby, 4 feet high: capsules rather acutely lobed, canescent with short somewhat scattered stellate pubescence: seeds smooth, lead-colored, 3 lines long. — Hacienda San Miguel (14).

*CROTON* —? Pistillate specimens only, closely resembling *C. gracilis*, but the styles very short and stout, and the broadly ovate seed much broader. — Frayles (288).

*CROTON* (*EUCROTON*) *TENULOBUS*. Monœcious; suffrutescent, much branched, the slender branches and petioles closely appressed-scurfy, the scales stellately parted to a disk-like centre: stipules obsolete; leaves linear-lanceolate, acute, obtuse and eglandular at base, lepidote beneath, greener above and rough with fine stellate pubescence, 1 to  $2\frac{1}{2}$  inches long; petiole 2 or 3 lines long: racemes short and shortly pedunculate: male flowers decandrous; pistillate flowers several, scattered, usually becoming reflexed and secund, on pedicels 2 lines long; calyx-lobes distinct, very narrow, lepidote,  $\frac{1}{2}$  to 1 line long, somewhat unequal: styles divided; capsule stellate-tomentose: seed oblong-ellipsoidal, obscurely reticulated,  $1\frac{1}{2}$  lines long. — Of Mueller's series *Argyrocroton*, as defined in Fl. Brasil., peculiar in appearance, and the pistillate flowers with characteristic calyx. Hacienda San Jose (29).

**MANIHOT** —? A small tree, 12 feet high and 2 or 3 inches in diameter, the few short branches leafy and fructiferous at the extremities: leaves 3 to 6 inches broad, round-cordate in outline, 7-lobed to much below the middle, the lobes entire, oblong-oblancoate, with a long setaceous tip: racemes short, axillary, few-fruited, the pedicels 9 to 12 lines long: capsule glabrous, 6 to 8 lines long: seed flattened ellipsoidal, 5 lines long. — Hacienda San Miguel (201).

**ACALYPHA CAROLINIANA**, Walt. — Same locality (133).

**ACALYPHA SUBVISCIDA**. Perennial, the slender herbaceous stems 1 to 2 feet high or more, branching, glandular-pubescent, as well as the petioles and inflorescence: stipules linear, deciduous; leaves ovate or more usually lanceolate, acute or acuminate, cordate at base, coarsely dentate, thin, nearly glabrous excepting the veins, 1 to 4 inches long, about equalling the petioles: spikes terminal and axillary, unisexual, loose, the staminate pedunculate, exceeding the petioles, the pistillate nearly sessile; bracts reniform, with about 13 short ovate teeth, 2 lines long in fruit or less: capsule subpubescent, muriculate above: seed smooth, dark,  $\frac{3}{4}$  line long. — Near *A. Schiedeana* and *A. conspicua*. Hacienda San Jose (39). Younger specimens from Hacienda San Miguel (17) seem to belong to the same species, though the bracts of the young pistillate flowers are very small, scarcely exceeding the ovary, and only 7-9-toothed, the middle tooth the larger. In both forms the fertile spike is often terminated by an abnormal pedicellate flower, in which the ovary consists of two (sometimes one) distinct cells lateral to the styles.

**DALECHAMPIA SCANDENS**, Linn. — Hacienda San Miguel (222).

**SEBASTIANIA** (?), *sp.* A many-stemmed shrub, 6 feet high, the specimens with undeveloped terminal flowering spikes and weather-worn 3-celled capsules: male bracts biglandular, 3-4-flowered; calyx 3-parted; stamens 3, distinct, alternate with the sepals: leaves oblong, acuminate, rounded at base, serrulate, 2 to 4 inches long. — Hacienda San Miguel (S); called "Yerba de la fleche," the juice being used for poisoning arrows. It has violent cathartic properties.

**FICUS** —? A tree 40 or 50 feet high by 6 feet or more in diameter: leaves round-obovate, slightly narrowed to an abrupt base, 2 or 3 inches long by  $1\frac{1}{2}$  or  $2\frac{1}{2}$  broad, on petioles 6 to 15 lines long: fruit sessile, small ( $\frac{1}{2}$  inch in diameter), edible. — Hacienda San Miguel, along gorges in the mountains (I); "Lageara."

**FICUS** —? A tree resembling the last: leaves oblong-lanceolate, very acute at both ends, 4 to 6 inches long on a petiole 9 to 16 lines long: fruit nearly globose, 10 lines in diameter, on a very short pedicel

(2 lines long), rather dry and chaffy within. — Same locality (L); "Chalate" or "Lalate."

*ALNUS ACUMINATA*, HBK. A tree, 20 to 30 feet high and 1 or 2 feet in diameter. — Cumbre (339), growing among pines and oaks. The bark is used for dyeing blankets.

*QUERCUS EMORYI*, Torr. A tree, 10 to 20 feet high and 1 to 1½ in diameter. — Yerba Buena (302), on poor grassy hills. The acorns are sweet, and much used by Indians and Mexicans.

*JUNIPERUS PACHYPHLOEA*, Torr. — A tree, 15 or 20 feet high and 2 or 3 in diameter. — Norogachi (UU); berries eaten.

*PINUS CHIHUAHUANA*, Engelm. A tree, 20 to 25 feet high and 1 or 2 in diameter: leaves 2 to 5 in the sheath: cones 2 to 2½ inches long. — Yerba Buena (301).

*PINUS CEMBROIDES*, Zucc. A "scrub pine," 20 or 25 feet high and 2 in diameter. — Yerba Buena (303).

*PINUS ENGELMANNI*, Carr. About 60 feet high and 3 to 5 feet in diameter, with short heavy branches: leaves usually in fours. — Norogachi (500). The specimens agree satisfactorily with Dr. Engelmann's description of the single specimen collected by Wislizenus in 1846. Palmer states that the Indians make of the cone a good and durable hair-brush by bruising off the corky portion of the scales.

*SPIRANTHES MADRENSIS*, Benth. & Hook.? The same as 1523 Coulter, 521 Pringle (1885) from near Chihuahua, and 477 Lemmon (1881) from Rucker Valley in Arizona. It agrees fairly well with Reichenbach's description of Seemann's plant from the Sierra Madre. — Norogachi (409).

*NOLINA* — ? Leaves only. — Hacienda San Miguel (241).

*DASYLIRION* — ? Leaves only. — Cumbre (340); the leaves are made into baskets, after removal of the spines.

*ECHEANDIA BREVIFOLIA*. Roots slender, thickened toward the ends: leaves spreading and subfalcate, 6 inches long and 4 or 5 lines broad: stem erect, 2 feet high or more, branching above, smooth, with several (about 6) appressed scarious bracts an inch long; floral bracts small: pedicels fascicled, jointed near the base, equalling the yellow flowers (6 lines long): capsule broadly elliptical, 3 lines long. — Distinguished from the ordinary species by the short falcate leaves, the more numerous cauline bracts, shorter capsules, etc. Hacienda San Miguel (229).

*COMMELINA VIRGINICA*, Linn., var. *ANGUSTIFOLIA*, Clarke. An unusually rough form. — Same locality (236).

**TINANTIA MACROPHYLLA.** Very finely pubescent throughout; stems somewhat succulent, 3 feet high: leaves oblong-ob lanceolate, narrowed to a broad cupulate-sheathing petiole, 6 or 8 inches long by 3 broad: peduncles terminal on short axillary branches, the unilateral cymes scarcely produced; bracts short; pedicels (2 to 4 lines long) and sepals (5 or 6 lines) densely pubescent: petals "creamy white, striped with purple": capsule oblong, equalling the sepals, the cells 5-seeded. — Hacienda San Miguel (184).

**BRAHEA CALCAREA,** Liebm.? In secluded cañons near Batopilas, 12 to 14 feet high and nearly a foot in diameter: leaves glaucous, very deeply palmately cleft and usually filiferous at the sinuses, the divisions bifid but not filiferous, the outer divisions very much reduced.

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Of the remaining endogens the Juncaceæ and Cyperaceæ have been named by Dr. N. L. Britton of Columbia College, and the Gramineæ by Dr. George Vasey.

**JUNCUS TENUIS,** Willd. — Hacienda San Jose (63<sup>a</sup>). **J. ACUMINATUS,** Michx. — Same locality (63<sup>b</sup>).

**CYPERUS FUGAX,** Liebm. — Same locality (63½). **C. INCOMPLETUS,** Link, very nearly. — Same locality (49). **C. FLAVUS,** Boeckl., var. **PEDUNCULARIS,** Britton. — Same locality (49½). The older name for this species is *C. flavamariscus*, Griseb. **C. SPECTABILIS,** Schreb. — Same locality (49¾). **C. DIANDRUS,** Torr., var. **CAPITATUS,** Britton. — Same locality (49<sup>a</sup>). **C. AMABILIS,** Vahl. (*C. glareosus*, Liebm.) — Same locality (49<sup>b</sup>). **C. ARISTATUS,** Rottb. — Same locality (49<sup>c</sup>).

**HEMICARPHA SUBSQUARROSA,** Nees. — Hacienda San Jose (63).

**RHYNCHOSPORA KUNTHII,** Nees. — Same locality (27).

**ERIOCHLOA LEMMONI,** Vasey & Scribner, *n. sp.* — Hacienda San Miguel (110<sup>a</sup>). **E. ARISTATA,** Vasey. — Same locality (110<sup>c</sup>).

**PANICUM FASCICULATUM,** Swartz. — Hacienda San Miguel (1<sup>a</sup>). **P. VELUTINOSUM,** Nees, var. (?) **MAJOR,** Vasey. — Same locality (1<sup>b</sup>). **P. DIVARICATUM,** Linn.? — Same locality (10). **P. CRUS-GALLI,** Linn., var. **MUTICUM.** — Same locality (18). **P. LEUCOPHÆUM,** HBK., var. **LACHNANTHUM.** (*P. lachnanthum*, Torr.) — Same locality (207). **P. PROLIFERUM,** Lam. — Haciendas San Miguel (1<sup>b</sup>) and San Jose (50). **P. SANGUINALE,** Linn. — Same localities (110<sup>f</sup>, 48).

**SETARIA LATIGLUMIS,** Vasey, *n. sp.* — Hacienda San Miguel (117<sup>a</sup>). **S. SETOSA,** Beauv. — Haciendas San Jose (52) and San Miguel (110<sup>d</sup>). **S. PAUCISETA,** Vasey, *n. sp.* — Hacienda San Jose (78).

**CENCHRUS ECHINATUS,** Linn. — Hacienda San Miguel (22).

*ÆGOPOGON GRACILIS*, Vasey, *n. sp.* — Hacienda San Jose (28).  
*Æ. GEMINIFLORUS*, HBK. — Hacienda San Miguel (153).

*CATHESTECUM ERECTUM*, Vasey & Haeckel. — Hacienda San Jose (66).

*ELIONURUS CANDIDUS*, Haeckel. — Norogachi (QQ).

*TRACHYPOGON POLYMORPHUS*, Haeck., var. (*T. Montufari*, Nees.)  
 — Hacienda San Jose (26).

*HETEROPOGON CONTORTUS*, Roem. & Schult. — Hacienda San Miguel (115<sup>b</sup>).

*ANDROPOGON SACCHAROIDES*, Swartz. — Same locality (2<sup>a</sup>). *A. CIRRHATUS*, Haeckel. — Same locality (7).

*CHRYSOPOGON NUTANS*, Benth., var. — Same locality (11).

*ARISTIDA SCABRA*, Kunth? — Same locality (115, 161). *A. ARIZONICA*, Vasey? — Same locality (5).

*MUHLENBERGIA SCHAFFNERI*, Fourn. — Hacienda San Miguel (3<sup>a</sup>).  
*M. GRACILIS*, Kunth, var. — Same locality (10<sup>a</sup>). *M. CAPILLARIS*, Kunth? — Same locality (13). *M. PALMERI*, Vasey, *n. sp.* — Same locality (16). *M. RAMOSISSIMA*, Vasey, *n. sp.* — Same locality (158).  
*M. ELONGATA*, Scribner, *n. sp.* — Same locality (159). *M. ARGENTEA*, Vasey, *n. sp.* — Same locality (160). *M. SPECIOSA*, Vasey, *n. sp.* — Hacienda San Jose (30).

*LYCURUS PHLEOIDES*, Kunth. — Hacienda San Miguel (2).

*SPOROBOLUS ANNUUS*, Vasey, *n. sp.* — Same locality (4). *S. RAMULOSUS*, Kunth. — Same locality (4<sup>a</sup>). *S. TRICHOLEPIS*, Torr. — Same locality (6). *S. SHEPHERDI*, Vasey, *n. sp.* — Same locality (9).  
*S. REPENS*, Kunth, var. — Same locality (17). *S. INDICUS*, R. Br. — Hacienda San Jose (29). *S. ASPERIFOLIUS*, Thurber. — Same locality (76).

*EPICAMPES MACROURA*, Benth.? — Hacienda San Miguel (1). *E. RIGENS*, Benth.? — Same locality (21).

*TRisetum DEYEUXIoidES*, Kunth. — Hacienda San Miguel (14).

*CHLORIS ELEGANS*, HBK. — Same locality (118).

*BOUTELOUA PROSTRATA*, Lag. — Same locality (3). *B. BROMOIDES*, Lag.? — Same locality (115<sup>a</sup>). *B. RACEMOSA*, Lag. — Same locality (206). *B. HIRSUTA*, Lag., var. — Hacienda San Jose (24).  
*B. ARISTIDOIDES*, Thurber. — Same locality (51). *B. JUNCIFOLIA*, Lag.? — Same locality (65).

*ELEUSINE INDICA*, Gaertn. — Hacienda San Jose (40). *E. ÆGYPTIACA*, Pers. — Same locality (73).

*LEPTOCHLOA MUCRONATA*, Kunth. — Hacienda San Miguel (117).

*COTTEA PAPPOPHOROIDES*, Kunth. — Same locality (162).

ARUNDO DONAX, Linn. — Hacienda San Jose (51\*).

ERAGROSTIS PURSHII, Schrad. ? — Hacienda San Miguel (8), and a var. (?) at Hacienda San Jose (508).

BROMUS CILIATUS, Linn., var. — Norogachi (PP).

The following cryptogamic plants of the collection were determined by Prof. D. C. Eaton.

NOTHOLÆNA SINUATA, Kaulf. The typical form. — Hacienda San Miguel (89).

NOTHOLÆNA ASCHENBORNIANA, Klotzsch. — Same locality (215).

NOTHOLÆNA CANDIDA, Hook. A form with very large but thin-fronds, evidently grown in the shade. — Same locality (82). Used by the Indians as a remedy in nephritic diseases.

NOTHOLÆNA LEMMONI, Eaton. The fronds somewhat narrower in outline than in the Arizona specimens. — Hacienda San Miguel (84), with yellowish powder on the under surface, and Norogachi (453).

NOTHOLÆNA NIVEA, Desv. — Hacienda San Miguel (215).

PTERIS AQUILINA, Linn., var. LANUGINOSA, Bong. — Norogachi (447).

PELLÆA SEEMANNI, Hook. Larger plants than 979 Parry & Palmer (1878), and showing some approach to *P. Skinneri*, Hook. — Hacienda San Jose (69).

PELLÆA TERNIFOLIA, Link. — Norogachi (452).

PELLÆA MARGINATA, Baker. — Norogachi (454), and a tall form with very narrow pinnules (446).

CHEILANTHES PRINGLEI, Davenport. — Hacienda San Miguel (116).

CHEILANTHES MICROPHYLLA, Swartz. — Same locality (86); also a form with ample fronds and large bright green pinnules, smooth on both surfaces, evidently due to the more shady place of growth (87).

CHEILANTHES WRIGHTII, Hook. — Same locality (88).

CHEILANTHES LEUCOPODA, Link. — Same locality (147).

CHEILANTHES LENDIGERA, Swartz. — Norogachi (444).

ASPENIUM TRICHOMANES, Linn. — Hacienda San Miguel (117).

ASPENIUM — ? A small tufted fern, probably a young plant of *A. cicutarium*, or other species of the same section. — Hacienda San Miguel (162).

ASPENIUM FILIX-FÆMINA, Bernh. A narrow form, nearly the var. *angustum* of the Ferns of North America. — Norogachi (451).

*ASPIDIUM PATENS*, Swartz. A small form, from among underbrush. — Hacienda San Miguel (161).

*ASPIDIUM JUGLANDIFOLIUM*, Kunze. The veins are free in these specimens. — Norogachi (450).

*CYSTOPTERIS FRAGILIS*, Bernh. — Norogachi (445, 449).

*WOODSIA MEXICANA*, Fée. — Norogachi (448).

*ANEIMIA ADIANTIFOLIA*, Swartz. — Hacienda San Miguel (91).

*SELAGINELLA CUSPIDATA*, Spring, and with it a form with leaves less cuspidate (*S. incana*, Spring). — Hacienda San Miguel (85).

*SELAGINELLA RUPESTRIS*, Spring. Nearly the var. *Mexicana*, Spring. — Same locality (92); also Norogachi (455), a form with spreading awnless leaves.

2. *Descriptions of New Species of Plants, chiefly from the Pacific States and Chihuahua.*

*CANBYA AUREA*. Dwarf, few-many-stemmed, with fleshy linear glabrous or sparingly pubescent leaves (1 to 3 lines long), clustered at the base, and naked scape-like peduncles  $\frac{1}{2}$  to 1 inch long: flowers bright orange, the petals ( $1\frac{1}{2}$  lines long) deciduous. — On the sagebrush plains of eastern Oregon; Thomas Howell, June, 1885, with the habit of *C. candida*, and its peculiar stigmas, varying from it in the color and deciduous character of the petals. Mature fruit was not found.

*THELYPODIUM HOWELLII*. Erect, slender, sparingly branched above, glabrous and glaucous, but the base of the stem and the radical leaves villous with spreading hairs: radical leaves oblanceolate, toothed or pinnatifid, an inch or two long, the cauline entire, lanceolate, sagittate and clasping: flowers scattered, ascending on short pedicels; calyx 2 or 3 lines long; petals narrowly linear, long-exserted: pods ascending, stipitate, slender, an inch long, tipped with a slender style. — Most nearly resembling *T. brachycarpum*. At Camp Polk and in Harney Valley, eastern Oregon; Thomas Howell, June, 1885.

*POLYGALA ACICULARIS*. Perennial, with stout branching caudex and numerous slender lax ascending somewhat fasciculate branched stems about a foot high, puberulent: leaves very numerous, alternate, sessile, narrowly linear, acuminate or acute, carinate, slightly puberulent or glabrous, 3 to 6 lines long: racemes sessile, short, few-flowered; flowers nearly sessile, white: sepals acute, the outer lanceolate, the inner oblong-ob lanceolate, twice longer, 2 lines long or more; wings oblong, obtuse; keel purple, with a white partly fimbriate crest exceeding the wings: fruit broadly elliptical, glabrous,  $1\frac{1}{2}$  lines long:

seed linear, slightly pubescent, the appendage of the hooded caruncle entire, oblong, nearly as long. — On calcareous ledges and banks in the Santa Eulalia Mountains, near Chihuahua; C. G. Pringle, May, 1885 (n. 233).

**SILENE HALLII.** Stems several from a thick caudex, usually low ( $\frac{1}{2}$  to  $1\frac{1}{2}$  feet high), glandular-pubescent, leafy: radical leaves linear-oblongate, the cauline linear, 2 to 4 inches long, finely pubescent, the floral shorter: flowers solitary or somewhat crowded in the axils, the lower peduncles more elongated: calyx oblong-ovate, with broad acute teeth, strongly nerved with purple or green, 6 lines long; petals purple, blade broad, bifid to near the middle, lobes somewhat oblique and unequal, with sometimes a blunt lateral tooth, appendages broad, entire or toothed, auricles broad, undulate, more or less ciliate: capsule ovate; stipe  $1\frac{1}{2}$  lines long. — In the Rocky Mountains of northern Colorado, alpine; collected by Hall & Harbour (1862, n. 61), E. L. Greene, above Golden City (1870), H. G. French, at foot of Pike's Peak (1874), T. S. Brandegee, on Mt. Princeton (1880), and H. N. Patterson, on Gray's Peak and vicinity (1885). It has been referred to *S. Scouleri*, from which it may be distinguished by its shorter and stouter stems, broader and shorter calyx, the form and color of the petals, and the broader capsule upon a shorter stipe.

**TALINUM BREVICAULE.** Roots very thick, branched and spreading: caudex somewhat branched, sending up very short herbaceous stems (about an inch high) scaly-bracted below, densely leafy and branching above: leaves sessile, terete, 3 to 6 lines long: peduncle about equalling the leaves, bearing 1 to 3 slender pedicels scarious-bracted at base: petals purple, obovate, 5 lines long, nearly twice longer than the obovate sepals: ovary ovate, the style a little shorter than the petals. — In the Santa Eulalia Mountains, Chihuahua; C. G. Pringle, May, 1885 (n. 26). With the habit of *T. brachypodum*. The older leaves on the dried specimens are inflated upon one side, the epidermis being completely separated from the parenchyma.

**ABUTILON MALACUM.** Apparently tall and suffrutescent, branching, very finely and closely velvety-pubescent throughout: leaves cordate, acute, acutely and somewhat unequally dentate,  $1\frac{1}{2}$  to 4 inches long and broad, about equalling the petiole: panicles axillary and terminal; pedicels jointed above the middle, 2 to 6 lines long in fruit, occasionally solitary in the axils and elongated: calyx cleft to or below the middle into lanceolate lobes, 3 or 4 lines long; petals twice longer, orange: carpels 5, oblong, acutish, coarsely stellate-pubescent, equalling the erect calyx. — Western Texas, collected in Wilson County

by Palmer, 1879 (n. 2139), in the Chenati and Vieja Mountains by Dr. V. Havard, 1881 (n. 8 and 130), and at El Paso by M. E. Jones, 1884 (n. 4193); on rocky hills near Chihuahua, C. G. Pringle, 1885 (n. 164, 363). Referred doubtfully, in Proc. Amer. Acad. 17. 331, to *A. Texense*, as a variety, from which species it differs in its stouter habit, denser inflorescence, the larger calyx not reflexed in fruit, the carpels more coarsely pubescent, etc.

**ABUTILON DUGESII.** Glutinous-pubescent throughout, suffrutescent: leaves ovate-lanceolate, acuminate, cordate at base, rather acutely dentate, densely stellate-tomentose,  $\frac{3}{4}$  to 2 inches long, the petioles nearly as long; stipules filiform: flowers axillary, solitary, on stout pedicels (4 to 12 lines long) jointed near the summit: calyx deeply cleft, the broad subacuminate lobes equalling the carpels; petals orange, 3 lines long: carpels 9, lanceolate, acuminate, finely stellate-pubescent, 6 lines long, 2-3-seeded. — Collected near Guanajuato by Berlandier in 1827 (n. 1330), and by Prof. A. Dugès, 1883.

**URVILLEA DISSECTA.** Stems herbaceous from a branching woody caudex or rootstock, 1 to 2 feet high, finely pubescent or glabrate, 8-sulcate, the alternate furrows deeper: leaves twice quinate, the larger about 3 inches long, the secondary petioles margined, the segments (3 to 6 lines long) pinnatifid or pinnately divided into 3 to 5 linear-oblong lobes, sparingly pilose and ciliate with short spreading hairs: peduncles equalling the leaves; flowers in short contracted panicles, ochroleucous, the calyx puberulent: fruit glabrous, inflated, thin-membranous, quadrangular in vertical outline, nearly twice broader than high (8 lines long), apiculate with the short style, abruptly short-cuneate at base, the large cells extending nearly to the base, compressed at the side and narrowly winged below; dissepiment above the attachment of the seed ovate in outline and broadly perforated: seed subglobose, 2 lines in diameter, attached near the base to the top of the thickened axis. — On cool slopes under cliffs near Chihuahua; C. G. Pringle, May and September, 1885, in flower and fruit (n. 8, 361 $\frac{1}{2}$ ). This was distributed under the name of *Serjania* (?) *dissecta*, on account of the apparent resemblance of the fruit to that of *Serjania cystocarpa*, Radl. (*S.* (?) *inflata*, Watson), mature specimens of which have not been collected. The mature fruit of the present species is essentially different, however, from that of *Serjania*, and does not differ greatly from that of *Urvillea*, to which genus therefore it is here referred.

**PSORALEA REVERCHONI.** Tall and branching (2 feet high), canescent with short appressed pubescence: leaves digitately 2-5-foliate;

leaflets linear-oblong, acute at each end, 6 to 12 lines long; stipules usually equalling the petiole, 1 to 3 lines long; flowers few, in short close racemes; bracts very broadly ovate and concave, abruptly acuminate: calyx 4 lines long, nearly equalling the petals, the long-acuminate lobes exceeding the tube. — Collected by J. Reverchon in 1877 on rocky prairies in Hood and Johnson Counties, western Texas, and distributed in Curtiss's sets as *P. cyphocalyx*, — from which it differs in its shorter leaves and petioles, shorter racemes, much broader bracts, and more deeply lobed calyx, etc.

*EYSENHARDTIA SPINOSA*, Engelm. Fruiting specimens collected by Pringle (n. 358) on hills near Chihuahua permit a more complete description of this remarkable species, previously found only by Wislizenus near Lake Encenillas in the same region. The leaflets are mostly retuse, puberulent beneath: flowers yellowish, the banner emarginate: ovary glabrous, the style very slightly pubescent; pod inequilaterally ovate in outline, 1-seeded, 2 lines long, the coriaceous convex valves strongly 2-3-nerved.

*DALEA VIRIDIFLORA*. Decumbently branching at the woody base, the herbaceous stems 6 inches high, glabrous throughout: leaves an inch long or less; leaflets small, 4 to 8 pairs, oblong-obovate, obtuse or retuse; stipules linear-setaceous: spikes sessile or shortly pedunculate, ovate to cylindrical,  $\frac{1}{2}$  to  $1\frac{1}{2}$  inches long; bracts lanceolate, narrowed at base, equalling the glabrous shining thin-scarious 10-nerved calyx, with very short acutely trifid teeth (pubescent on the inside) and large glands between the nerves; petals yellowish green, half longer than the calyx: style slightly villous; pod glabrous. — Summit of the Santa Eulalia Mountains, Chihuahua; C. G. Pringle, November, 1885 (n. 518).

*DALEA PLUMOSA*. Suffrutescent, the slender ascending stems branching above, finely pubescent and dotted with minute black glands, a foot high: leaves an inch long or less; leaflets 5 to 8 pairs, oblong-obovate, obtuse or retuse, 2 or 3 lines long, somewhat soft-pubescent; stipules brown, lanceolate: spikes pedunculate, an inch long; bracts ovate-lanceolate, glabrous, exceeding the calyx-tube, deciduous: calyx-tube campanulate, glabrous, thin, 10-nerved, with 2 to 4 black glands in the intervals, the long filiform teeth and inner margin plumose with long hairs; petals yellow becoming brownish, the keel 4 lines long: pod villous, short. — In the shade of cliffs near Chihuahua; C. G. Pringle, October, 1885 (n. 621).

*PETALOSTEMON SABINALIS*. Perennial, the herbaceous simple stems a foot high, glabrous throughout: leaves yellowish green;

leaflets 5 to 7 pairs, linear, obtuse, narrowed at base, about  $\frac{1}{2}$  inch long: spikes rather slender, pedunculate, 2 inches long or less; bracts very narrow and attenuate, deciduous, equalling the calyx: calyx campanulate, somewhat scarious below, thicker and glandular above, with short triangular acute teeth pubescent on the inner side; petals rose-color fading to nearly white, twice longer than the calyx: pod glabrous. — Collected by J. Reverchon in Bandera County, Texas, at the entrance to Sabinal Cañon, June, 1885 (n. 45).

**PETALOSTEMON REVERCHONI.** Perennial, with numerous slender ascending stems 6 inches high or less, finely pubescent: leaves glabrous or the petiole slightly pubescent; leaflets 2 to 5 pairs, linear, acutish, subrevolute, 2 to 5 lines long: spikes sessile or nearly so, very short or becoming 2 inches long: calyx covered with fine appressed pubescence, the acuminate teeth nearly equalling the tube; petals deep pink or red, a half longer: pod silky-pubescent. — On the rocky top of Comanche Peak, in western Texas; J. Reverchon, June, 1882 (n. 36).

**ASTRAGALUS PRINGLEI.** Near *A. Cobrensis*; annual, procumbent, much branched from the base (stems 6 inches long or less), canescent with very fine appressed pubescence: leaves 1 or 2 inches long; leaflets 5 to 7 pairs, linear to oblanceolate, obtuse, 1 to 3 lines long, finely silky-pubescent both sides or glabrous above: racemes numerous, short-pedunculate, about equalling the leaves, loosely few-flowered: calyx tubular, 2 lines long, with short narrow teeth; petals pink, 5 lines long, the narrow keel erect: pod 2-celled, chartaceous, oblong, straight, sessile, deeply and at length broadly sulcate on the back, the ventral suture not prominent, 3 to 5 lines long, ascending, pubescent. — Plains near Chihuahua; C. G. Pringle, April, 1885 (n. 79).

**ASTRAGALUS MISELLUS.** Of the *Galegiformes* group, perennial, with numerous ascending herbaceous stems (6 inches high), canescent throughout with short appressed pubescence: leaves (an inch or two long) with 8 to 10 pairs of small linear-oblong leaflets: peduncles about equalling the leaves, few-flowered: flowers spreading or reflexed: calyx campanulate, the narrow teeth nearly equalling the tube; petals yellowish, twice longer (3 or 4 lines): pod linear, somewhat curved, attenuate to a stipe a little longer than the calyx, compressed, 2-celled and Y-shaped in section, rather narrowly sulcate on the back, acute on the ventral edge, reflexed, finely pubescent, 8 to 10 lines long. — Near *A. Howelli*, but a much smaller and smaller-flowered species, and with a shorter, more shortly stipitate pod. Collected near Mitchell, Wasco County, Oregon; Thomas Howell, May, 1885.

**ASTRAGALUS DIURNUS.** Of the *Inflat*i section; apparently perennial, many-branched from the base, the ascending stems (6 inches high) slender, somewhat appressed-pubescent: leaves (1 or 2 inches long) of about 5 pairs of obovate, obtuse, or retuse leaflets, glabrous above, pubescent beneath, 1 to 3 lines long: peduncles shorter than the leaves, slender, few-flowered; flowers spreading or reflexed, pale yellow or lined with purple, 3 lines long; calyx turbinate-campanulate, the slender teeth as long as the tube: pod inflated, 1-celled, membranous, sessile, obliquely oblong-ovate, the ventral edge nearly straight, somewhat compressed, finely pubescent, about 8 lines long. — Most nearly related to *A. subcinereus* and *A. Wardii*. Collected at Dayville, on John Day River, Oregon, by Thomas Howell, May, 1885.

**ASTRAGALUS (SCYTOCARPI) QUINQUEFLORUS.** Annual, prostrate, many-branched at base, the very slender stems (6 inches long or less) canescent with short appressed straight pubescence: leaves elongated; leaflets 3 to 5 pairs, linear to linear-oblong, obtuse, 2 to 6 lines long: peduncles elongated; raceme short, loosely few- (usually 5-) flowered: flowers white or purplish,  $2\frac{1}{2}$  lines long; calyx turbinate, the subulate teeth as long as the tube: pod chartaceous, 1-celled, sessile, oblong, turgid, somewhat compressed and the sutures nearly flat, pubescent, 5 lines long. — On the hills and plains near Chihuahua; C. G. Pringle, April, 1885 (n. 234).

**LATHYRUS NUTTALLII.** Stout and tall, more or less pubescent throughout with loose woolly hairs: stipules semi-sagittate, rather narrow; leaflets 3 to 6 pairs, variable, narrowly or broadly elliptical, usually acute or acutish at both ends, apiculate, 1 or 2 inches long; rhachis tendril-bearing: peduncle shorter than the leaves, few-flowered: calyx-teeth triangular, acuminate, the lower somewhat larger; petals reddish purple, 6 to 8 lines long: pod glabrous, oblong, attenuate to a very short thick stipe, 1 to  $1\frac{1}{2}$  inches long by 4 lines wide: seeds globose, brown. — First collected by Nuttall in "Upper California," and frequently since by various collectors, from British Columbia (Telegraph Trail, lat.  $54^{\circ}$ , J. Macoun, and Vancouver Island, C. B. Wood) to Oregon and western Idaho (Clear Water, Spalding). It has been usually referred to the eastern *L. venosus*, which is not found west of the Rocky Mountains.

**CÆSALPINIA SESSILIFOLIA.** Shrubby, 4 to 6 feet high, glabrous throughout, the younger branches green and somewhat glaucous, with a pair of straight or recurved prickles at or below the nodes: leaves of a single pair of pinnæ, closely sessile, with a pair of stipular prickles; secondary petioles about an inch long, with stipellar

prickles; leaflets 2 or 3 pairs, ovate-elliptical, obtuse, 3 to 6 lines long: racemes terminal, short; pedicels 3 or 4 lines long, usually subtended by a pair of prickles: flowers 4 lines, long; filaments villous: ovary and style glabrous: pod rhombic-oblong, very shortly stipitate, 3-seeded, an inch long. — Collected by Dr. Gregg at Bolson de Mapimi, 1847, and in Coahuila by C. G. Pringle, on hills and mesas about Jimulco, May, 1885 (n. 202).

**HOFFMANSEGGIA MULTIJUGA.** Herbaceous, rather stout, 2 or 3 feet high, covered throughout (excepting the leaflets) with small black substipitate glands: pinnæ 6 to 10 pairs; leaflets 5 to 8 pairs, oblong, finely pubescent on the margin, glandular-pitted beneath, 1 to 4 lines long; stipules entire: racemes axillary, exceeding the leaves (6 to 10 inches long), many-flowered; bracts ovate, acuminate; pedicels jointed in the middle, 2 or 3 lines long in fruit: sepals and petals 3 or 4 lines long: pods oblong-rhombic, obliquely acute at each end, black-glandular and somewhat pubescent, an inch long, 2-seeded. — Hillsides near Chihuahua; C. G. Pringle, May and August, 1885 (n. 138, 371).

**HOFFMANSEGGIA FRUTICOSA.** Shrubby, about 6 feet high, with brown bark, the slender branchlets, foliage, and inflorescence canescent with fine pubescence: stipules lacinate; leaves small, with 1 or 2 pairs of pinnæ; leaflets 3 or 4 pairs, oblong, obtuse, an inch or two long, glandular-dotted beneath, as also the petioles: racemes terminal, shortly pedunculate, 2 inches long in fruit; bracts lacinate; pedicels slender, jointed near the summit: calyx and petals  $2\frac{1}{2}$  lines long: pod lunate, an inch long, finely pubescent, dotted with small black sessile glands. — In mountain cañons near Jimulco, Coahuila; C. G. Pringle, April, 1885 (n. 230).

**BAUHINIA (CASPARIA) UNIFLORA.** A large shrub, with grayish-brown bark: stipules obsolete; petioles short, bifoliate, apiculate; leaflets coriaceous, obliquely obovate, rounded or retuse above, cuneate at base, 2-nerved and reticulately veined, somewhat puberulent or glabrous, 3 to 5 lines long: flowers solitary, terminal, or apparently lateral, shortly pedicellate; calyx puberulent; petals purple, 9 or 10 lines long, with greenish subtomentose claws: sterile stamens connate at base, subtomentose,  $1\frac{1}{2}$  lines long, the fertile glabrous and nearly equalling the petals: ovary tomentose, long-stipitate, beaked with a long style. — In cañons near Jimulco, Coahuila; C. G. Pringle, April, 1885 (n. 174). Closely resembling *B. ramosissima*, Benth., in habit, differing in the shorter petioles, smaller 2-nerved leaflets, solitary flowers, much shorter sterile stamens, etc.

**MIMOSA (ACANTHOCARPA) PRINGLEI.** A low erect much-branched slender shrub, armed with short recurved infrastipular spines: leaves very finely pubescent, glabrous above; petioles short (1 or 2 lines); pinnae a single pair; leaflets 2 pairs, oblong-elliptical, 1 to  $1\frac{1}{2}$  lines long or less: flowers in globose heads on short (3 lines) axillary peduncles, glabrous, tetramerous; stamens 8: pod glabrous, unarmed or sparingly aculeate on the margin, somewhat curved, an inch long, the thin valves not jointed. — Allied to *M. flexuosa*. On rocky hills east of Chihuahua; C. G. Pringle, October, 1885 (n. 545).

**MIMOSA (ACANTHOCARPA) PROLIFICA.** A stout erect shrub, 4 to 6 feet high, with stout straight infrastipular spines (4 or 5 lines long): petioles with short recurved prickles and pubescent with short spreading hairs, not glanduliferous; pinnae 6 to 9 pairs, with usually a small rigid spine-like gland near the base; leaflets 12 to 17 pairs, narrowly oblong, acute, ciliate or nearly glabrous,  $1\frac{1}{2}$  to 2 lines long: flowers in a globose head upon an axillary peduncle (9 lines long), glabrous, pentamerous; stamens 10: pods numerous, linear, curved, aculeate on the margins, not jointed,  $1\frac{1}{2}$  to 2 inches long by 2 lines wide, covered with minute brownish resinous dots. — On rocky hills west of Chihuahua; C. G. Pringle, April and August, 1885 (n. 208, 372). Near *M. Grahami*.

**ACACIA BIACICULATA.** Stems prostrate and slender, 1 to 3 feet long, from a short thick caudex, appressed-pubescent, armed with very slender straight whitish stipular spines,  $\frac{1}{2}$  to 1 inch long: petioles pubescent, glandular between the lower pinnae, an inch long or less; pinnae 1 to 4 pairs; leaflets usually 10 pairs, narrowly oblong, glabrous, a line long: peduncles axillary, solitary, equalling the leaves: flowers in small heads, glabrous, orange-colored: pod linear, more or less falcate, flattened and somewhat torulose, finely pubescent, 9 to 18 lines long and 2 broad; valves thin. — Near *A. constricta*, but of very peculiar habit. On sandy plains near Chihuahua; C. G. Pringle, August, 1885 (n. 662).

**ACACIA ANISOPHYLLA.** A small tree, sparingly armed with short straight scattered spreading spines, pubescent: petioles puberulent, glanduliferous; pinnae 1 to 3 pairs; leaflets 4 to 7 pairs, oblong, obtuse, the terminal pair broadest (2 to 5 lines), glabrous, 3 to 7 lines long: flowers capitate, the peduncles racemose: pod coriaceous, with thickened margins, flattened, somewhat curved, stipitate, glaucous, 4 inches long by an inch wide. — Resembling *A. Rømeriana*, but the heads racemose and pods very much thicker. In mountain cañons near Jimulco, Coahuila; C. G. Pringle, May, 1885 (n. 163).

**APIUM (AMMOSELINUM) BUTLERI**, Engelm. in herb. A low glabrous annual, branching from the base: leaves ternate-quinate, the short segments narrowly oblong: umbels sessile opposite to the leaves, the rays and pedicels very short (2 or 3 lines or less); involuclers of 1 to 3 narrow bracts: petals entire, concave: fruit ovate, acute, a line long, strongly ribbed, the ribs acute and smooth or slightly scabrous, and the lateral ribs continuous over the commissure as a thin corky margin; seed semiterete, slightly concave on the face and somewhat channelled beneath the solitary vittæ of the intervals. — Texas, in wet grounds near Houston, E. Hall (n. 244), March, 1872, and near Dallas, J. Reverchon, March and April, 1874; Indian Territory, south of the Arkansas, G. D. Butler, 1876. It has been distributed as *Apium Popei* both in Hall's Texan collection and in the sets of A. H. Curtiss, but differs in the nearly sessile umbels and in the much smaller and smoother fruit, the corky commissural margin of which is much less developed.

**FERULA PURPUREA**. Nearly acaulescent, the 2 or 3 stout stems (about a foot high) from a thick root: leaves few, glabrous, large and very much dissected, the ultimate segments linear and often short: rays 8 to 20, becoming 3 or 4 inches long; involuclers of several linear acuminate bracts: flowers purple: fruit elliptical, 9 to 12 lines long by 5 wide, about equalling the pedicels, with a thick corky margin and numerous vittæ. — On rocky hillsides near the lower Columbia River; in Klickitat County and the Simcoe Mountains, Washington Territory, collected by W. N. Suksdorf and the Howell Brothers, and at Hood River in Oregon by Mrs. P. G. Barrett.

**PEUCEDANUM COUS**. Acaulescent, from a nearly globose tuber ( $\frac{1}{2}$  to 1 inch in diameter), glabrous or very slightly puberulent: leaves quinate-pinnate, the leaflets 3-5-parted or -cleft or sometimes entire, the segments linear-oblong (2 to 4 lines long): scapes exceeding the leaves (3 to 6 inches high), roughish; rays unequal (2 inches long in fruit, or less); involuclers of about 12 short oblong-ovate scariously margined bracts: flowers yellow: fruit nearly sessile, somewhat puberulent, oblong to rather broadly elliptical, strongly ribbed, 3 or 4 lines long; vittæ filling the broad intervals. — Eastern Oregon; collected in John Day's Valley by Thomas Howell (n. 270), May, 1880, and at Antelope (n. 418), and by W. C. Cusick (n. 358) in Union County. The plants are known to the Indians as "Cous," and the roots collected for food.

**PEUCEDANUM CUSICKII**. Dwarf, caulescent (apparently from a branching rootstock), glabrous: leaves once or twice ternate, the seg-

ments with 3 to 5 linear acute lobes (3 or 4 lines long): stem exceeding the leaves (2 to 4 inches high), bearing a single leaf and an umbel of 1 to 3 short fertile rays; involucels unilateral, of 2 or 3 narrow acuminate bracts: fruit very shortly pedicellate, oblong-elliptical, 4 or 5 lines long, the thin wings as broad as the body; vittæ narrow, solitary in the intervals, 4 to 6 on the commissure. — On the highest summits of the Eagle Creek Mountains, Union County, Oregon; W. C. Cusick, September, 1885, in fruit. Flowers probably white. Resembling small forms of *P. simplex*, but the leaf-segments ternate or quinate, and the vittæ more than a single pair on the commissure.

**PARONYCHIA WILKINSONI.** Perennial, with numerous stems from the branching caudex, puberulent throughout: stems  $1\frac{1}{2}$  to 3 inches high, with numerous very short nodes: leaves linear-subulate, nerveless, attenuate from near the base to the pungent apex, 2 or 3 lines long, the narrow scarious stipules as long and at length spreading: flowers in close terminal cymes,  $1\frac{1}{2}$  lines long, the white awns half the length of the sepals and soon spreading. — On gravelly hills south of Chihuahua, first found by Edward Wilkinson, a collector in natural history at that place; C. G. Pringle (n. 341). Resembling *P. Jamesii*, from which it differs especially in the much shorter internodes, the attenuate nerveless leaves with comparatively longer stipules, the larger flowers, and longer and more spreading awns.

**IREGINE LAXA.** Herbaceous, tall (3 to 5 feet high) and slender, tomentose: leaves lanceolate, acuminate, rounded or slightly cuneate at base, shortly petiolate, densely tomentose beneath, greener and finely pubescent above, 3 to 5 inches long, those upon the very slender and lax flowering branches very narrowly lanceolate and more attenuate at base, an inch or two long: heads of flowers small, alternate and mostly pedunculate along the opposite branchlets of the diffuse panicle, only the uppermost nearly sessile: bracts villous-pubescent, equalling the densely long-silky perianth; staminate flowers unknown. — In shaded places in the Jimulco Mountains, Coahuila; C. G. Pringle (n. 141), April, 1885.

**ERIOGONUM JONESII.** Of the *Corymbosa* group, a woody-based branched tomentose perennial,  $2\frac{1}{2}$  feet high or less: leaves alternate, ovate, white-tomentose beneath, greener above, the blade  $\frac{1}{2}$  to  $1\frac{1}{2}$  inches long, shorter than the petiole: bracts subtending the open dichotomous corymb, somewhat foliaceous: involucre mostly sessile and solitary, tomentose, scarcely a line long: flowers a line long, slightly exserted, glabrous, white or pinkish, the inner sepals oblong, the outer obovate and emarginate. — Collected at Cosnino, Arizona, a station on the

Atlantic and Pacific Railroad, near the San Francisco Mountains; Marcus E. Jones, August, 1884.

**EUPHORBIA LINEATA.** Of the *E. hypericifolia* group, perennial, the herbaceous stems from a subterranean branching rhizome, slender, ascending, several times branched, pubescent, a foot high: leaves obovate or oblong-ovate, oblique, obtuse or acutish, rounded at base or the lower cuneate, pellucid between the fine reticulations, entire or sparingly serrulate, 6 to 9 lines long: cymes a terminal pair, usually shortly pedunculate, loose: involucre pubescent, turbinate,  $\frac{1}{2}$  line long; lobes lacerate; glands 4, stipitate, with a small oblong white appendage: capsule pubescent, acutely lobed,  $\frac{1}{2}$  line long: seed quadrangular-ovate, obscurely rugose or subtuberculate. — On the grassy borders of warm springs near Chihuahua; C. G. Pringle (n. 187), April, 1885. Near *E. pycnanthema*, which is glaucous, with acute leaves, more conspicuous appendages to the involucre, larger glabrous capsules, and an oblong rugose seed.

**STILLINGIA BICARPELLARIS.** Shrubby, 3 or 4 feet high, glabrous, with slender light-colored stems and branches: leaves alternate, linear-lanceolate, somewhat falcate, acute, cuneate at base upon a very short petiole, glandular-denticulate, 1 to  $2\frac{1}{2}$  inches long: spikes terminal, sessile, short, with several sessile pistillate flowers at base, frequently reduced to a single pistillate flower; bracts broadly ovate, glanduliferous: staminate calyx campanulate, crenately toothed; stamens 2; pistillate calyx of 2 broad ovate sepals: stigmas 2, thick, linear, spreading: capsule broadly ovate, acute, the 2 cocci separating from a stout 2-horned gynophore without columella, 4 lines long: seed subglobose, with or without a very small strophiole. — In the Jimulco Mountains, Coahuila; C. G. Pringle (n. 128), May, 1885. In some respects very similar to *Sebastiania* (?) *bilocularis*, but differing in habit, the glanduliferous bracts, calyx, gynophore, etc.

**CALOCHORTUS LYONI.** Near *C. nitidus*; stems branching and somewhat flexuous, 1 or 2 feet high, bearing several leaves and 2 to 4 or more solitary flowers: sepals naked, acute; petals lilac or purplish, with a darker purple sparingly brown-villous spot at base surrounding the short-oblong hairy gland, 12 to 20 lines long: anthers oblong-elliptical, obtuse,  $1\frac{1}{2}$  to 2 lines long: capsule narrowly elliptical, obtuse, 3-winged, nearly an inch long. — Los Angeles County, California; collected on hills near Los Angeles by W. S. Lyon and Dr. Gray, and at Newhall by Dr. Gray, in 1885.

3. *Notes upon Plants collected in the Department of Yzabal, Guatemala, February to April, 1885.* — I. *Ranunculaceæ to Connaraceæ.*

From the 25th of February to the 20th of April, 1885, I was in the department of Yzabal in eastern Guatemala, and spent a considerable portion of this time in collecting such plants as were found in flower or fruit. So little is critically known respecting the flora of this region that my collection of about five hundred species should be of somewhat more than ordinary interest. The following account of so much of it as I have yet had time to examine will show how far this expectation is likely to be realized. The full set is to be found in the herbarium of Harvard University; few duplicates were made.

The entrance to Guatemala from the east has always been by the Rio Dulce, which breaks through the hills bordering the coast and allows passage to light steamers and other craft to Lake Yzabal, and thence up the Polichic River, a hundred miles into the interior. The valley of the Rio Dulce is hemmed in closely on the south side by the Sierra Mico, a low broken range separating it from the valley of the Motagua, and terminating near the coast in the peak of San Gil, about 3,700 feet in height. At the mouth of the river is the town of Livingston, situated on a bluff overlooking the roadstead, with low ground on each side along the sea and river. Beyond the tortuous, picturesque, precipitously walled gorge by which the Dulce pierces the hills it opens out into the Gulfetta, with a low densely wooded valley on the northern side, through which flows the Chocon River, a short deep stream heading in the hills beyond. Upon this river, about thirty miles by boat from Livingston, is the plantation recently opened by the Tropical Products Company of Boston, where, through the courtesy of its President, W. T. Brigham, Esq., I spent most of the month of March.

Above the Gulfetta the river-banks again contract until the entrance to Lake Yzabal is reached, where stands the dilapidated fort of San Felipe, built by the Spaniards to protect the interior towns from the depredations of the buccaneers. On the southern shore of the lake is the town of Yzabal, very pleasantly situated on high ground, and the eastern terminus of the *Camino Real*. This long-used highway, passable, like all roads in Guatemala, only upon foot or on horseback, crosses over the Sierra Mico into the Motagua valley by a pass of about 1,500 feet altitude, and then turns westward toward the city of Guatemala. At Yzabal, through the generous hospitality and kind assistance of Thomas J. Potts, Esq., a fortnight was profitably passed

(after a week of malarial fever) in excursions along the lake and into the mountains, made the more successful by the hearty and vigorous co-operation of his father-in-law, A. W. Lanier, Esq., of La Grange, Tennessee, himself a well-informed botanist, whose seventy years rest lightly upon him. My visit to Guatemala was concluded by a three days' trip to the Motagua valley and the ruins of Quirigua.

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1. *CLEMATIS AMERICANA*, Mill. A puberulent form of this polymorphous species (as it is now generally considered), with 3-foliate sparingly pubescent leaves, the large thin entire leaflets broadly ovate; the inflorescence somewhat more pubescent, with mostly digitately divided bracts; achenes nearly glabrous. On the Camino Real near Yzabal.

2. *DAVILLA RUGOSA*, Poir. A tall shrub on river-banks at Livingston and Chocon.

3. *DAVILLA LUCIDA*, Presl? Leaves thinner, with the margins not at all revolute, more acuminate, and acute at base, not shining above; petals none. At the Chocon plantation. This species is referred by Hemsley to *D. Kunthii*, St. Hil.

4. *DOLIOCARPUS PUBENS*, Mart. A tall shrub on the river-bank at Livingston.

5. *CURATELLA AMERICANA*, Linn. The "sandpaper tree," the firm rough leaves being used as a substitute for sandpaper in polishing woodwork. On dry hills at El Mico, near Quirigua.

6. *TETRACERA* —? A very scabrous climber: leaves broadly oblong or oblong-ovate, acute, rounded at base, denticulate toward the apex, scabrous both sides, with usually some stellate hairs above and appressed hairs on the narrowly-winged petiole, 2 to 4 inches long: staminate panicles loose, scabrous; bracts narrowly lanceolate: sepals 5, nearly equal, rounded, scabrous-puberulent and scantily hairy on the outer side, puberulent within, 2 lines long; petals 5; stamens very numerous, short. — Apparently an undescribed species, but only staminate specimens collected. On the banks of the Chocon.

7. *GUATTERIA JURGENSENI*, Hemsl. Berries numerous upon the receptacle, oblong, 4 lines long, about half the length of the slender stipe. This seems to be Hemsley's species, as described by him. Shores of Lake Yzabal, in fruit; also collected by W. T. Brigham at Chocon, in flower and fruit.

8. *GUATTERIA* —? Branches slender, glabrous: leaves coriaceous, smooth and shining, narrowly oblong-lanceolate, acuminate, nar-

rowed into a short petiole (2 lines long), 3 or 4 inches long or more: peduncle terminal, nearly an inch long: berries numerous, 6 lines long, about equalling the stipe. — Apparently undescribed; locality uncertain.

9. *ANONA PALUSTRIS*, Linn. A low straggling tree, on the sea-shore near Livingston.

10. *XYLOPIA FRUTESCENS*, Aubl., var. *GLABRA*. Glabrous, or the younger leaves sparingly appressed-villous beneath. — A shrub, on the shores of Lake Yzabal; in fruit. Similar to specimens collected at Panama by Hayes (n. 121) and Seemann, and in Venezuela by Fendler (n. 1306).

11. *CISSAMPELOS TROPÆOLIFOLIA*, DC.? According closely with the descriptions and Delessert's figure, except that the fruit has a double ridge on each side, formed (in the skeleton) of flattened radiating processes, and the hairs upon the leaves are longer and looser. The fruit is red at maturity. Near Yzabal, along the Camino Real.

12. *CISSAMPELOS PAREIRA*, Lam.? Staminate specimens only: leaves round-reniform, not peltate, lighter-colored beneath with very fine appressed pubescence; flowers mostly umbellate upon the ultimate branches of the inflorescence. Banks of the Rio Dulce, below the Gulfetta.

13. *NYMPHÆA AMPLA*, DC. In the Polichic River, above Lake Yzabal.

14. *CLEOME POLYGAMA*, Linn. About Fort San Felipe.

15. *ALSODEIA GUATEMALENSIS*. A shrub, puberulent upon the branchlets, petioles, and inflorescence: leaves opposite, glabrous or the veins slightly pubescent, oblong-oblancheolate, more or less acuminate, attenuate at base, slightly crenate or entire, 2 to 4 inches long, the slender petiole 3 lines long: racemes terminal, usually shorter than the leaves; pedicels slender, spreading, jointed near the base, 1 or 2 (in fruit 3) lines long: sepals broad-lanceolate,  $\frac{1}{2}$  line long: ovary obovate, pubescent, obtuse, the slender style over a line long; ovules solitary; fruit 6 lines long, the valves acute, the placenta and seeds glabrous. — On the banks of the Chocon River. Resembling *A. flavescens*, Spreng., as figured by Aublet and described by Eichler, differing especially in its pubescence, obtuse pubescent capsule, and solitary seeds; flowers not seen.

16. *SAUVAGESIA ERECTA*, Linn. On the Camino Real pass over the Sierra Mico.

17. *ONCOBA LAURINA*, Oliver. (*Mayna laurina*, Benth.) The seed has a broad basal hilum, and a thick fleshy reddish aril covering

the whole inner face. A small tree, on the banks of the Chocon and the shore of Lake Yzabal.

18. *CASEAREA (PIPAREA) BRIGHAMI*. A small tree with pubescent branches: leaves oblong-oblongeolate, rather abruptly and narrowly acuminate, narrowed to a very short petiole, entire, glabrous and shining above, puberulent beneath, 6 to 10 inches long and 2 to 4 broad, thin-coriaceous, not punctate: flowers in dense axillary clusters; pedicels slender (3 to 6 lines long), jointed in the middle, pubescent with spreading hairs below the joint, tomentose above: sepals 5, ovate, 2 lines long (becoming 5 in fruit): stamens 18, twice longer than the inner whorl of linear villous staminodia: ovary pubescent; style trifid: fruit dry, triangular-obovate, 6 lines long, 1-few-seeded: seed slightly villous. — At the Chocon plantation.

19. *POLYGALA ASPERULOIDES*, HBK. Near Yzabal. This species can scarcely be referred to *P. galioides*, as is done by Bennett and Hemsley. It resembles *P. verticillata*, but is perennial and with broader leaves. *P. galioides*, of Guiana and Brazil, is an annual, with smaller flowers in a much more slender elongated open spike, and much smaller capsules and seeds.

20. *DRYMARIA CORDATA*, Willd. In wet places on the shore of Lake Yzabal.

21. *CLUSIA* —? A large tree in the Chocon forests; only pistillate specimens collected. Glabrous; leaves coriaceous, opposite, oblanceolate, obtuse, narrowed to a stout petiole ( $\frac{1}{2}$  inch long or more), 4 or 5 inches long: flowers solitary and terminal on a bibracteate peduncle, the broadly ovate segments of the perianth decussate in pairs, the petals 5 lines long: immature capsule oblong (15 lines long), 6-valvate; the stigmas broad and peltate upon short and very thick styles.

22. *CLUSIA* —? A low wide-branching tree, in a potrero at Yzabal; called a gutta-percha tree. Leaves opposite, thick-coriaceous, oblong-obovate, very obtuse, attenuate to a stout petiole (an inch long), 6 or 7 inches long: peduncle axillary, short, bearing a few flowers upon stout bracteate pedicels: segments of the perianth decussate in pairs, rounded; fertile flowers with 4 stamens; ovary 6-valved and bearing 6 broad peltate sessile stigmas.

23. *SYMPHONIA GLOBULIFERA*, Linn. f. (*Moronobea coccinea* of Grisebach; the hog-gum tree of Jamaica.) Leaves unusually short and narrow (2 or  $2\frac{1}{2}$  inches long and 5 or 6 lines broad); immature fruit oblong-ovate, beaked by the stout style, by abortion 2-celled and 2-seeded. A large tree in the Chocon forests.

24. *CALOPHYLLUM* (?), sp. Leaves resembling those of *Calophyllum* in venation and appearance, oblong, rounded above with a short oblong obtuse apex, cuneate at base, 3 or 4 inches long, on a slender pedicel: fruit solitary on a stout axillary peduncle, subglobose, an inch long, dehiscent by five (?) very thick fleshy valves. — A tree in the Chocon forests. The dehiscence of the fruit would remove it from *Calophyllum*.

25. *MARCGRAVIA RECTIFLORA*, Triana & Planch., var. *GOUDOTIANA*, Triana & Planch. A shrub, at Chocon, with oblong acute leaves, rounded at the base and nearly sessile, 3 or 4 inches long; bracts not seen.

26. *SIDA RHOMBIFOLIA*, Linn. At the Chocon plantation.

27. *PAVONIA RACEMOSA*, Swartz. A tall shrub on the banks of the Rio Dulce.

28. *HIBISCUS ABELMOSCHUS*, Linn. Edges of woods on the Camino Real above Yzabal.

29. *GOSSEYIUM BARBADENSE*, Linn., as defined by Todaro. A tall shrubby plant in a yard at Livingston. Leaves with 3 or 5 long-acuminate lobes: capsule oblong-ovate, narrowly acuminate, over two inches long: seeds 9 in each cell, easily separated from the fibre, 6 lines long, the fibre twice longer.

30. *PACHIRA* —? A tall tree upon a rocky limestone hill at the Chocon plantation; only flowers collected. Calyx glabrous, truncate, 5 lines long; petals  $3\frac{1}{2}$  inches long, narrow, finely pubescent, the hairs near the base longer and reflexed, rough-puberulent within and villous with reflexed hairs toward the top: staminal tube very short, villous, the filaments (nearly 3 inches long) connate in pairs and pentadelphous at base. — Another species, with very large fruit, probably *P. macrocarpa*, is common on the banks of the Rio Dulce.

31. *HAMPEA* (?) *STIPITATA*. A large tree, the branchlets, petioles, and pedicels scabrous with a dense tangled stellate pubescence: leaves ovate, somewhat acuminate, truncate or subcordate at base, digitately 5-nerved, entire, roughly stellate-pubescent beneath, nearly smooth above, 6 or 7 inches long on petioles 2 or 3 inches long: fruiting pedicels (1 to 4) fascicled in the axils, 8 to 12 lines long; bractlets minute, deciduous: calyx turbinate, distinctly 5-lobed, 3 lines long: capsule globose, 6 to 8 lines broad, on a glabrous stipe equalling the calyx-tube, scabrous, 3-valved, the valves thick-coriaceous, slightly villous on the inner margin and lined with a close white fibrous coat: seeds 2 in each cell, ascending, not collateral, glabrous, half-covered and coherent by a partially adherent aril; albumen thin: cotyledons

unequal, the larger enfolding the smaller. — Banks of the Chocon. The foliage closely resembles that of *H. integerrima* except in its pubescence; the fruit is more like that of *H. thespesioides*. It differs from both in the lobed calyx and stipitate capsule. The cotyledons are punctate with numerous black oil-cells, as in *Gossypium*, *Ingenhousia*, and *Thespesia*, with which the genus should be placed rather than with the *Bombacæ*.

32. *HALICTERES GUAZUMÆFOLIA*, HBK. On the Sierra Mico.

33. *BYRSONIMA CRASSIFOLIA*, Kunth. A cultivated tree at Yzabal, 20 or 30 feet high; leaves loosely villous-tomentose beneath, nearly glabrous above; flowers abundant, yellow, turning red.

34. *BUNCHOSIA LANIERI*. A tree, with the somewhat compressed branchlets, the peduncles and pedicels, the petioles and lower surface of the leaves canescent with closely appressed silky malpighiaceae hairs: leaves thin, elliptical or elliptic-lanceolate, acutish at both ends, glabrous above, glandless, 4 to 7 inches long on petioles 3 or 4 lines long: racemes solitary or in pairs, 3 inches long; pedicels jointed near the base, 4 lines long in fruit: calyx 8-glandular: drupe red, subglobose, 5 or 6 lines in diameter, slightly pubescent, 3-celled, with a thin chartaceous endocarp, 1-3-seeded. — On the Camino Real near Yzabal.

35. *STIGMAPHYLLON LUPULUS*. A vine, covered excepting the glabrous upper surface of the leaves with a more or less dense sub-tomentose pubescence of branching hairs: leaves rarely ovate, usually cordate and deeply hastate-lobed, 4 or 5 inches broad, the lobes lanceolate, acuminate, entire or sparingly toothed, the basal divaricate or ascending, the petiole an inch long, biglandular near the blade: peduncles stout, exceeding the leaves; pedicels 6 or 8 lines long in fruit: stigmas foliaceous: samaras appressed-silky,  $1\frac{1}{2}$  inches long, 3-costate on each side, and the wing often with a dorsal tooth. — Scarcely woody, running over the ground and climbing bushes in the clearings at the Chocon plantation.

36. *HIRÆA* — ? Leaves opposite, oblong-oblancoelate, shortly acuminate, cordate at the narrowed base, glabrous, shining above, paler beneath, the midvein puberulent, without glands or with minute marginal glands near the apex, 4 to 6 lines long, the short petiole with a pair of linear stipule-like appendages in the middle: inflorescence silky-puberulent; peduncles solitary or in pairs, umbelliferous: calyx glandless; petals concave, unequal, the larger shortly fimbriate, the smaller one with glandular fimbriæ. — Much resembling *H. fagifolia* of Brazil. Locality uncertain, but probably Chocon.

37. *HIRÆA RECLINATA*, Jacq.? Closely resembling Trinidad specimens of this species, except that the peduncles and pedicels are less villous and the calyx very conspicuously glandular. Banks of the Rio Dulce.

38. *OXALIS DENDROIDES*, HBK. On the pass over the Sierra Mico, at 1500 feet altitude.

39. *OURATEA* (*GOMPHIA*) *GUATEMALENSIS*, Engler, var.? Differing from the description in the narrower leaves (4 to 7 inches long and  $1\frac{1}{2}$  or 2 broad), and shorter stipules: the subpaniculate raceme is 2 or 3 inches long: fruit obovate (3 lines long), solitary upon the smaller globose gynophore, the pedicel 4 lines long. A small shrub in the forests at the Chocon plantation.

40. *MELIA AZEDARACH*, Linn. Naturalized about Yzabal.

41. *GUAREA BIJUGA*, C. DC.? Leaflets 1 or 2 pairs, oblong-elliptical, abruptly narrowly acuminate, acute at base, 4 to 8 inches long and  $2\frac{1}{2}$  broad, the petiole and rhachis 2 to 4 inches long: panicle sessile, very short and few-flowered: flowers glabrous or nearly so, tetramerous; calyx-lobes very short, acute: fruit obovate, reddish, coriaceous, 8 lines long, the pedicel very short. A small tree on the banks of the Chocon.

42. *XIMENIA AMERICANA*, Linn. On the river-bank at Livingston.

43. *WIMMERIA DISCOLOR*, Schlecht. Banks of the Rio Dulce.

44. *HIPPOCRATEA OVATA*, Lam. A form with thin oblong obscurely crenate leaves, mostly narrowed from above the middle to the obtuse base. A shrub, on the banks of the Rio Dulce.

45. *GOUANIA TOMENTOSA*, Jacq.? Leaves oblong-ovate, mostly broadest above the middle, acuminate, broadly cordate at base, acutely serrate, rufous-tomentose beneath, slightly pubescent and darker above, 2 or 3 inches long: fruiting racemes elongated, paniculate. A shrub, on the banks of the Chocon.

46. *VITIS* (*CISSUS*) *LANCEOLATA*. Stem rough with scattered tubercles: leaves simple, narrowly lanceolate to ovate, acuminate, rounded or cuneate at base, or the broader somewhat truncate, with about 6 pairs of nerves excurrent into short acute teeth, 3 to 5 inches long, the slender petioles  $1\frac{1}{2}$  to  $2\frac{1}{2}$  inches long: panicles about equaling the petioles, thrice dichotomous: fruit obovate, acute or acutish, 4 to 7 lines long; seed solitary, large, the albumen sharply angled, rugose and more or less deeply ruminant. — On the banks of the Rio Dulce and of the Chocon. Distinguished from all forms of *V. sicyoides* by its long petioles and by the size and shape of the fruit.

47. *VITIS SICYOIDES*, Benth. & Hook., var. *OVATA*, Baker. Leaves oblong-lanceolate, acuminate, more or less narrowly cuneate at base. Shores of Lake Yzabal.

48. *VITIS VULPINA*, Linn., var. (?) *YZABALANA*. Leaves ovate-cordate, coarsely toothed, with a long-attenuate acumination, glabrous, shining beneath, 2 to 4 inches long, a scant cobwebby pubescence upon the young leaves; petioles puberulent, about half the length of the blade or less (6 to 18 lines): tendrils simple: panicles small, shorter than the petioles, pubescent: petals and stamens 5 or 6. — On the lake-shore near Yzabal; fruit unknown. In *V. vulpina* the round-cordate leaves are not acuminate and about equal the smooth petioles in length.

49. *SERJANIA MEXICANA*, Willd. Nearly glabrous: stem deeply furrowed: leaves biternate, with minute glandular puberulence and scantily villous beneath; leaflets oblong-lanceolate, cuneate at base, with one or two blunt teeth each side of the acutish apex, 3 or 4 inches long: inflorescence an elongated axillary naked divaricately branched panicle ( $1\frac{1}{2}$  feet long); sepals densely tomentose. — Banks of Chocon River.

50. *CARDIOSPERMUM GRANDIFLORUM*, Swartz, var. *HIRSUTUM*, Radl. Structure of the flower identical with that of Jamaica specimens of the species. Stem and petioles loosely covered with long spreading somewhat rigid hairs. Near the shore of Lake Yzabal.

51. *ANACARDIUM OCCIDENTALE*, Linn. Cultivated and naturalized; at Livingston, on Cayo Paloma in the Gulfetta, and frequent along the shore of Lake Yzabal.

52. *SPONDIAS LUTEA*, Linn. Foliage only, resembling in every respect that of this species. A tall tree in the Chocon forests,  $1\frac{1}{2}$  feet in diameter, with hard dark-colored wood; known as "Mulatto-wood."

53. *SPONDIAS* —? A tree in the Chocon forests, with glabrous foliage; leaves a foot long; leaflets 12 pairs, thin, rather abruptly long-acuminate, attenuate to a slender petiole, the sides very unequal, 2 or 3 inches long. Called "Maho" by the workmen.

54. *ROUREA GLABRA*, HBK. A vine, climbing by tendrils; shore of Lake Yzabal.

55. *CONNARUS POTTSII*. A shrub, 8 or 10 feet high, glabrous throughout: leaves trifoliate, thin-coriaceous, oblong, abruptly short-acuminate, rounded at base, 4 inches long, the wrinkled petiole 3 lines long: racemes crowded upon the short terminal peduncle, 4 inches long or less; pedicels short (a line long in fruit): sepals glabrous (or glabrate?): fruit solitary, on a short stipe (a line long), somewhat obcom-

pressed, oblique, strongly gibbous on the dorsal side and projecting beyond the short acute beak on the ventral side, finely striate, 8 lines long: seed black. — Much resembling *C. Turczaninowii*, Hemsl., which has more numerous leaflets on shorter petioles, and the fruit upon a twice longer stipe, not striolate, compressed and semicircular, the dorsal suture being nearly straight. Shore of Lake Yzabal; the fruit is said to be used as a poison for dogs.

#### 4. Notes upon some Palms of Guatemala.

Of the twenty-five species of palms collected by me in Guatemala, most still remain undetermined. The following notes upon a few of the more prominent, but rarely collected and hitherto little known, will be of interest.

*ATTALEA COHUNE*, Mart. This is the most conspicuous palm on the bottom lands of the Chocon River and along the Rio Dulce, and probably attains the largest size of any native species in Guatemala. It is known as the Cohune, Monaco, or Corozo palm, these names being variously applied to different stages of its growth. For a series of years it remains acaulescent and barren, its huge leaves rising nearly erect from the ground. Even after the trunk has reached a height of ten or fifteen feet or more, and has long been in bearing, it usually remains covered to the ground with the persistent bases of the sheathing petioles. Finally, these are gradually dropped, and the tree shows a clean cylindrical trunk of thirty to fifty feet or more. The finest specimen of this kind that I saw was in an opening upon the wooded flanks of the Sierra Mico near Yzabal.

The blade of the leaf is fifteen to twenty feet long, vertical in position, and describing a most graceful curve, its numerous divisions entirely distinct (an inch broad or more and an inch or two apart) and conduplicate at base. The leaves are used for thatching, but are much inferior to the less divided and flatter leaves of the *Manicaria*. The triangular rhachis is higher than broad, to which the vertical position of the leaf is due, its upper surface rufous-tomentose, as well as the folded edges of the unexpanded blade. The persistent spathes are pendent from among the leaves, six or seven feet long, very thick and firm, and of the color and appearance of sole-leather, glabrous, deeply many-sulcate for the whole length excepting the slender beak. The slender branches of the sterile spadix are a foot long, bearing the flowers mostly in pairs in the axils of broad triangular bracts. The inflexed petals of the staminate flowers are six or eight lines long. In the fer-

tile spadix the large flowers are crowded upon the short stout branches (three inches long), the cuspidate petals fifteen lines long, little exceeding the sepals; ovary pubescent, three-celled, more than half covered by the pubescent campanulate or suburceolate disk (five lines deep). The fruiting spadix is loaded with five to eight hundred or more nuts, which are elliptic-ovate, and two and a half inches long, not including the broadly conical beak. The thick bony endocarp encloses usually a single seed, sometimes two or rarely three. There can be little doubt that this palm is the *Cocos lapidea* of Gaertner (Fruct. 1. 16, t. 6, f. 1), at least as collected by Karwinsky between Oaxaca and Zacatepec, and described by Martius in Palm. Orbign. 104, and Hist. Palm. 3. 290, t. 167, f. vii.

**ACROCOMIA VINIFERA**, Oersted. A handsome palm, twenty to thirty feet high or more, very frequent in the forests of the Motagua valley near Quirigua. A single tree was seen near Yzabal, from which specimens were secured. The stem is cylindrical, erect, armed with erect black rigid flattened spines (two to six inches long), and covered above by the sheathing bases of dead persistent leaves. The long pinnate leaves have the leaflets arranged in two ranks on each side of the rachis, and are dark green and shining above, and glaucous and villous beneath. The spathes are numerous among the leaves, about four feet long and three or four inches in diameter, very densely fuscous-setose and armed with scattered pubescent spines (an inch or two long, or less), and terminating in a slender beak (four inches long). The branches of the spadix are stout at base, bearing six to ten pistillate flowers, the more slender upper portion staminate, with the alveolæ ciliate-tufted at the angles: ovary and young fruit densely covered with dark brown appressed pubescence; mature fruit glabrous, subdepressed-globose, nearly two inches in diameter, the nut an inch in diameter. The species is clearly distinct from *A. sclerocarpa*, but it may be the same as *A. Mexicana*, Mart., which is known only from Karwinsky's brief description and the figure reproduced by Martius (Hist. Palm. 3. 285, t. 138). At Yzabal it is known as "Coyol," the same name which Oersted (who alone has collected it) found given to it on the western side of Nicaragua and in Costa Rica.

**MANICARIA PLUKENETII**, Griseb. & Wendl. ? This is a common palm in the densely wooded low grounds along the sea-shore near Livingston. As seen there the trunk is usually ten or fifteen feet high, and about six inches in diameter, covered with the bases of dead leaves; rarely thirty feet high, but less than a foot in diameter, the lower part of the trunk naked and very deeply scarred. They often

stand in clusters of three to five together. The blade of the leaf is about twelve or fifteen feet long, rounded and bifid at the apex, very irregularly divided, the segments being unequal in width and either approximate or more or less remote, sometimes coherent toward the margin. The primary veins are about six or eight lines apart; the usually lanceolate teeth for the most part bi-dentate; the rhachis triangular or rhomboidal in section, acute above, flat or more or less carinate beneath, rufous-tomentose or glabrate. The spathes are several from among the lower living leaves, two feet long or less, thin-fibrous to the acute apex, persistent over the fruit; the long peduncle compressed. The spadix is rufous-tomentose, with ten to twenty simple branches which together are twelve to eighteen inches long; staminate calyx about two lines long, half the length of the oblanceolate acute petals; pistillate flowers usually solitary on each branch, the lanceolate petals six or seven lines long; ovary beaked by the upright stigmas (two lines long), smooth, but the thin epidermis soon broken away, and the surface becoming densely muriculate. The fruit is simple, double, or triple, covered with acute pyramidal gibbosities, globose when simple, and two inches in diameter; nut brownish black, fifteen lines in diameter.

This is probably the same species that, as found in Trinidad, is imperfectly described by Grisebach (Fl. Brit. W. Ind. 518), and it is pretty clearly distinct from *M. saccifera*, Gaertn. What is called the upper spathe by Bentham & Hooker, and the lower spathe by Drude, was the only one observed. The upper membranous spathe of Drude's description (Fl. Bras. 3<sup>2</sup>. 518) is probably only an empty bract, of which there are usually several upon the enclosed peduncle. This palm is known at Livingston as the "Confra Palm," and its leaves are used exclusively for thatching. Of all the full-grown fruit collected by me on the 20th of April, but very few were found to be mature.

*BACTRIS BALANOIDEA*, Wendl. This species, as respects the pistillate flowers and fruit, is well described and figured by Oersted under the name of *Augustinea balanoidea* (Vidensk. Middel. 1858, 39, and L'Amer. Centr. t. 9, fig. 1-13). The foliage is described and figured equally well under *A. ovata*, and there is little reason for believing that the two are distinct. It is frequent near the shore of Lake Yzabal, where it is known by the name of "Poknobo," and its tough slender stems are much used by the natives in the walls of their houses. It is gregarious, growing to a height of eight or ten feet, with a diameter of an inch or more, covered with numerous black

spines from two to four inches long. The regularly pinnate leaves have the flattened-quadrangular pubescent rhachis similarly armed; the segments aculeolate upon the margins, about an inch apart, a foot long by eight lines wide, acuminate, one side produced about an inch beyond the other. The spathe, about a foot long, is densely aculeate (excepting the narrow base), and the peduncle of the spadix is black with densely crowded prickles. The roughish nut is irregularly oblong, with one pore near the oblique summit, and the other two near the middle, their margins more prominent than they are figured by Oersted.

**BACTRIS COHUNE.** Stems erect, straight and slender, six to fifteen high, covered with the persistent sheaths of dead leaves and armed with numerous black and shining flattened spines (often a half-inch broad and two inches long or more). Leaves irregularly pinnate, glaucous beneath, the petiole and rhachis (convex beneath, prominently ridged above) tomentose and armed; segments very unequal, often distant, long-attenuate (three feet long), sparingly aculeolate on the margin, the primary veins about six lines apart. Spathes several, eight to twelve inches long, white-tomentose, the base and slender acumination unarmed, the inflated portion (six inches long) covered with black slender flattened spines six lines long. Spadix branched, armed at base, the pistillate flowers sessile on the rhachis, the staminate covering for their whole length the numerous very slender branches (two or three inches long). Staminate calyx very thin and densely woolly; petals lanceolate, united at base, over two lines long; stamens four. Calyx and corolla of the pistillate flowers somewhat aculeate, coriaceous, urceolate, dentate; corolla six or eight lines long; calyx nearly half as long; disk none. Ovary aculeate, acuminate, 3-celled; style stout; stigmas very short. Fruit densely prickly, nearly two inches long, narrowly obovate, somewhat attenuate above and beaked; the somewhat fibrous pericarp and more woody endocarp not separable, scarcely a line in thickness, 1-celled; seed obovate, acute at base, rounded above, an inch long, the surface reticulated; embryo near the summit.

This palm, which does not appear to be nearly allied to any described species of the genus, is abundant in the Chocon forests, and is called the "Warree Cohune" from the resemblance of its fruit in shape to those of the *Attalea*, and in their bristly covering to the "warree" or white-lipped peccary of the country. It is also called "Lancetia," from the lancet-shaped spines with which the stem is covered. The fruit is eatable, and is much more easily broken than that of the co-

hune, the pulp of both resembling in flavor that of the cocoa-nut. The characters of the fruit are in some respects quite peculiar, but they do not differ essentially from those of the genus.

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\* \* \* Omitted on page 454.

ERIOGONUM ORDII. Belonging to the *E. pusillum* group: diffusely branching from the base, 1 to 2 feet high, the leaves and lower part of the stems thinly floccose-tomentose: leaves broadly elliptical, obtuse, attenuate at base, the blade 1 or 2 inches long: pedicels filiform and elongated, spreading, in a very diffuse panicle; involucre narrowly turbinate, glabrous,  $\frac{1}{2}$  line long or less: flowers white or tipped with pink, very pubescent, a line long in fruit, the sepals narrow. — On sand-dunes near Fort Mohave in western Arizona; collected by J. G. Lemmon in April, 1884, and at his suggestion named for Dr. J. L. Ord, U. S. A., surgeon at the post, through whose aid Mr. Lemmon's collections were made in that region. In the inflorescence and fruit it much resembles *E. inflatum*.

## XXVI.

NOTES ON ARCTIC ALGÆ; BASED PRINCIPALLY  
ON COLLECTIONS MADE AT UNGAVA BAY BY  
MR. L. M. TURNER.

BY W. G. FARLOW.

Communicated May 12, 1886.

IN 1883, Dr F. R. Kjellman communicated to the Swedish Royal Academy a monograph of "The Algæ of the Arctic Sea," which has since been issued as a separate publication. No botanist has ever had such advantages for acquiring a knowledge of Arctic Algæ as Dr. Kjellman, who accompanied Nordenskiöld in several of his voyages, and his admirable treatise must form the basis of any study of Arctic forms. Those interested in the literature relating to the Algæ of Greenland and the Arctic shores of the eastern coast of America will find a complete account in Dr. Kjellman's work. In the present connection, it is my object to give a summary of the species of marine algæ collected by American explorers in Arctic regions in recent years, especially those of a date subsequent to the completion of Dr. Kjellman's great work.

The largest of the collections was that made by Mr. L. M. Turner at Ungava Bay in 1884. It included a considerable number of mounted specimens, besides some rough-dried material, which was soaked out and mounted subsequently. This collection is especially interesting because it contains a number of species of *Florideæ* which are seldom seen in herbaria. Not only are the species themselves of great interest, but they are here represented, in several cases, by large sets of specimens, which enable one to estimate the amount of variation in specific characters. This is a point of considerable importance, for, except in rare cases, only a very small number of specimens of the less common *Florideæ* are to be found in Arctic collections.

I have also examined a second collection, made by Dr. Ludwig Kumlien, the botanist of the Howgate Polar Expedition in 1877-78, which includes some interesting *Phæosporeæ*. The algæ collected by

Dr. Kumlien were determined by me provisionally, and a rough list was printed in the Bulletin of the National Museum, No. 15 (Washington, 1879); but, not supposing that my list was to be published, the specific names were given without naming the authorities. In the following account, I have included a revision of the algæ collected by Dr. Kumlien, which were mostly found at localities comparatively near Ungava Bay. As they are of interest in studying the distribution, I have added occasional notes of some of the forms received from the coast of Alaska, collected by Mr. John Murdoch, the botanist of the expedition to Point Barrow, under Lieutenant Ray, and of some species from St. Paul's Island near Behring's Straits, for which I am indebted to Prof. D. C. Eaton.

### FLORIDEÆ.

#### ODONTHALIA DENTATA, Lyngb.

Ungava Bay (Turner). A large number of specimens were collected, all of the broad form common on the northern shores of Europe. The narrow form of this species which, were it not for intermediary forms, might almost be considered a distinct species, is apparently more common in the Gulf of St. Lawrence than the type. The typical form was collected at Point Barrow, and was also found as far south as Victoria, British Columbia, by Mr. G. W. Lichtenhaler, one of whose specimens was unusually broad, being almost flabellate in shape. On the eastern coast this species is unknown south of Halifax, N. S.

#### POLYSIPHONIA ARCTICA, J. G. Agardh.

Ungava Bay (Turner). Annanactu Harbor, Gulf of Cumberland (Kumlien). A considerable number of specimens were collected, and, in all those examined, a section of the larger branches showed seven cells surrounding a central cell. The specimens from Annanactu Harbor grew on kelp at a depth of seven fathoms.

#### RHODOMELA LYCOPODIODES, J. G. Ag., var. TENUISSIMA, Kjellman.

Ungava Bay (Turner). Penny Harbor (Kumlien).

The typical form of this species as figured in the Phycologia Britannica, and represented in Areschoug's *Algæ Scandinaviæ Exsiccata*, No. 3, is unknown to me on the American coast. Several specimens, which agree closely with a specimen of Ruprecht's *Fuscaria tenuissima*, which is considered by Kjellman a variety of *R. lycopodioides*, were collected both by Turner and Kumlien. A coarser

form, which I can with difficulty distinguish from some of the New England forms usually placed in *Rhodomela subfusca*, Ag., were found at Kikkerton Island by Kumlien.

DELESSERIA SINUOSA, Lamour.

Evidently as common in the Arctic Ocean as on the coasts of Europe and New England, and represented by a very large number of specimens collected by the present expedition.

DELESSERIA MONTAGNEI, Kjellman.

The present name was adopted by Kjellman in his Algæ of the Arctic Sea, in order to distinguish *Del. denticulata*, Montagne, from Harvey's species of the same name. A large number of specimens, which can be referred without doubt to *Del. denticulata*, Mont., were collected at Ungava Bay. They are sufficiently distinguished at sight from *Del. alata* by the serrated margin of the fronds. Besides, the lateral veins are with a lens generally easily seen in the broader parts of the fronds, thus agreeing with the description given by Kützing in the *Tabulæ Phycologicæ*. With regard to the relationship of the alga from Ungava Bay to *Del. spinulosa*, Rupr., a species found in the Pacific, I am unable to express any opinion, as in none of the North Pacific collections which I have examined is there any form resembling the present species.

DELESSERIA ALATA, Lamour.

A number of specimens which seem without doubt to belong to this species were collected at Ungava Bay. They resemble closely the broader form of the species found on the British coast. A few small specimens resembling rather the common narrow form of the New England coast than the type, were found on *Ptilota serrata*, collected by Kumlien. *Delesseria angustissima*, Griff., a species certainly closely related to *Del. alata*, must be very rare on the American coast, if it occurs at all. A single specimen, collected several years ago at Cape Ann, by Mrs. Lusk, and referred by me to *Del. angustissima*, has cystocarpic fruit. Unfortunately the specimen was somewhat water-worn when collected, and, on that account, the determination is somewhat uncertain.

DELESSERIA BAERII, Rupr.

DELESSERIA CORYMBOSA, J. G. Ag.

The members of the subgenus *Cryptoneura* are, with one exception, very difficult to distinguish. This arises in part from the small

number of specimens of this group which are to be found in herbaria. An extraordinary number of specimens, not far from 150, were collected at Ungava Bay, and with this large amount of material it may be possible to obtain a better knowledge of the variations of the species of this group than has hitherto been possible. Some of the material was mounted, and the rest was kept rough-dried and soaked out by me for examination. The specimens furnished an abundance of tetraspores, and in some cases cystocarps. Some of them were from six to eight inches long, the fronds arising from a disk-like base as far as could be judged from the small number of specimens in which the base was present. In general the specimens could be arranged in two sets, although transitional forms were unfortunately frequent, and I am almost forced to believe that they are all forms of a single species, but what to call that species it is not easy to decide. In one set the main axis bears a number of long lateral branches, which are comparatively thin and compressed and more or less regularly zigzag, giving off the short secondary branches at the angles. The ultimate branches are short and distichously pinnate, becoming somewhat corymbose at the tip. There can be little doubt that the specimens just described should be placed in *Delesseria corymbosa*. The figure of that species in Kjellman, *loc. cit.*, Plate X. fig. 3, resembles closely the specimens from Ungava Bay, although the plant figured is somewhat smaller and narrower than ours.

The first set of specimens to which I have referred suggest in habit some of the forms of *Microcladia Coulteri*, Harv., of our west coast. The fronds of the specimens of the second set are less compressed, and the ultimate branches are more attenuated, so that, in some cases, they resemble somewhat forms of *Ceramium rubrum*. The arrangement of the cystocarps and tetraspores is the same in both sets of specimens. A small number of specimens similar to those now placed in the second set were collected on kelp in six fathoms, at Annanactu Harbor, by Kumlien, in October, 1877, and were referred by me to *Delesseria rostrata*, J. G. Ag. A specimen was afterwards examined by Professor Agardh, who thought that it was *Del. Baerii* rather than *Del. rostrata*. Certainly the Ungava Bay alga resembles the figure of *Del. Baerii* in Kützing's *Tabulæ Phycologicæ*, drawn from a specimen in Herb. Sonder, and also a specimen from Nova Zembla collected by Kjellman. *Del. Baerii*, first described from the Arctic Pacific region, extends as far as Spitzbergen, but is not credited to Greenland or the eastern coast of America. *Del. rostrata*, Ag., based on Lynghye's *Gigartina purpurascens*, var. *rostrata*, is a Green-

land form, and apparently Ruprecht doubts whether it is distinct from his *Del. Baerii*. By Agardh and Kjellman the two are kept distinct. Certainly one is not warranted in expressing a definite opinion from an examination of the figures of *Del. rostrata* in Lyngbye and the Flora Danica, for they are too imperfect to be recognized with certainty. On the whole, I am inclined to regard all the specimens from Ungava Bay as forms of a single species, because there are several specimens which connect the two sets already described. So far as they can be divided into two sets, I should consider them to belong in part to *Del. corymbosa*, and in part to *Del. Baerii*, on the grounds above stated, and the copious material from Ungava Bay warrants one in asking whether the two species in question are really distinct. A single specimen of what is here called *Del. Baerii* was found at Prince Edward's Island, in a collection received from Mrs. A. L. Davis.

DELESSERIA JÜRGENSII, J. G. Ag.

DELESSERIA CRASSIFOLIA, Rupr.

These two characteristic Algæ of the North Pacific were found in a collection from St. Paul's Island, Behring's Straits, received from Prof. D. C. Eaton.

RHODYMENIA PALMATA, Grev.

Ungava Bay (Turner 423 and 4870). Large specimens of the typical form. Although this species has been recorded in several works as occurring in the North Pacific, it is extremely doubtful whether such is the fact. All the Pacific specimens referred to this species which I have seen have proved, on microscopic examination, to belong to *Callophyllis*, or other genera than *Rhodymenia*.

RHODOPHYLLIS VEPRECUA, J. G. Ag. (*Fucus dichotomus*, Lepechin.)

Ungava Bay (Turner, 447, 765, 809, and 4872), Annanactu Harbor. On rocks at low tide, October, 1877, and Ovifak, Greenland, August, 1878 (Kumlien).

Typical forms. The broadest specimens which I have ever seen were collected on the coast of Massachusetts.

EUTHORA CRISTATA, J. G. Ag.

Ungava Bay (Turner). Annanactu Harbor, on rocks at low tide. (Kumlien). Common as is this species on the New England coast, our Arctic collectors have brought home but few specimens. The single small specimen from Ungava Bay had cystocarpic fruit. Most

of the specimens of Kumlien belong to the narrow form, and grew at low-water mark. A specimen from forty fathoms is eight inches long, with broad ultimate divisions.

HALOSACCION RAMENTACEUM, J. G. Ag.

But few specimens of this common species were collected, and none of them were at all equal to New England specimens in luxuriance of growth. The specimens of *Phyllophora membranifolia* mentioned as collected by the Howgate Expedition in the Bulletin of the National Museum, No. 15, are in reality narrow forms of *H. ramentaceum*.

PHYLLOPHORA INTERRUPTA, J. G. Ag.

Fine typical specimens of this species were collected at Point Barrow, but only a single specimen appears in the collection from Ungava Bay.

KALLYMENIA PENNYI, Harv.?

Ungava Bay (Turner, no. 451 and 4873). Two small portions of a *Kallymenia* were among the mounted specimens, and there were besides several much larger specimens in the rough-dried material, some of which bore cystocarpic fruit, so that there can be no doubt of the generic determination. None of the specimens showed any trace of a stipe or a point of attachment. The more perfect were nearly a foot in diameter, and deeply and irregularly lobed at the circumference, the general outline being somewhat oval. Some of the fronds were perforated with a few holes, the largest of which were half an inch in diameter, but the majority were much smaller. The holes were evidently not the result of erosion or decay, but similar to the holes which normally appear in the fronds of certain Algæ. The color was the same as in British specimens of *K. reniformis*, but the thickness of the fronds was somewhat greater than in that species, although it should be added that different authentic specimens of *K. reniformis* vary considerably in thickness.

The present form certainly is not *K. ornata*, P. & R., which has a different color, substance, and habit, and, in spite of the existence of perforations in the frond, I think it must be referred either to *K. reniformis* or *K. Pennyi*. With regard to the last-named species, the descriptions are hardly sufficient to enable one to distinguish it with accuracy, and the question arises whether it may not, after all, be a luxuriant Northern form of *K. reniformis*. *K. Pennyi* was originally found in the Gulf of Cumberland, and in all probability the specimens from Ungava Bay may be referred to the same species, whether

that is really distinct from *K. reniformis* or not. Specimens of *Kallymenia* are among the rarities of the Atlantic coast of America, and the genus is known on the New England coast only from a single specimen collected near Boston by Mr. F. S. Collins. The Ungava Bay specimens are large, and apparently belong to mature plants; but, in the absence of a stipe and a set of younger specimens, the determination may be questioned.

*PTILOTA PECTINATA*, Kjellm.

Under this name, Kjellman, in his Algæ of the Arctic Sea, includes the *Ptilota serrata* of Agardh, and the *P. plumosa* var. *serrata* of Kützing, as the type form of the species first described in Gunner's Flora Norvegica as *Fucus pectinatus*. A large number of specimens were collected at Ungava Bay, which are identical with the common New England form. There were besides a small number of specimens which may be referred to the variety *integerrima*, Kjellman, *loc. cit.*, Plate XV. fig. 1.

*CALLITHAMNION AMERICANUM*, Harv.

Ungava Bay (Turner, no. 449, 770, and 820).

*CALLITHAMNION PYLAISÆI*, Mont.

Ungava Bay (Turner). Gulf of Cumberland (Kumlien).

*CALLITHAMNION* (*ANTITHAMNION*) *BOREALE*, Kjellman, var.  
*CORALLINA*, Kjellman?

A single specimen collected at Ungava Bay may perhaps be referred to this species, but the material was not sufficient to enable me to speak with confidence.

*RHODOCHORTON ROTHII*, Naeg.

In the account of the Algæ of the Howgate Expedition this species is reported from the Gulf of Cumberland. The specimen was sterile, and the determination necessarily doubtful.

*DIPLODERMA MINIATUM*, Kjellman.

The genus *Diploderma* of Kjellman includes the species of *Porphyra* whose fronds consist of a double layer of cells. Among the rough-dried specimens from Ungava Bay was a large specimen which can with very little doubt be referred to the present species. Naturally, algæ of this genus are much injured by resoaking; but, in spite of the unsatisfactory state of the specimens when mounted, a micro-

scopic examination when they were soaked out for preparation showed that the measurements agreed with those of *Porphyra miniata*.

### FUCACEÆ.

A few specimens of *Fucus* were collected at Ungava Bay, but they were all sterile and otherwise in too unsatisfactory condition to be determined.

### PHÆOSPOREÆ.

#### LAMINARIA LONGICRURIS, De la Pyl.

A single small specimen from Ungava Bay, with a fragment of another unrecognizable species of the genus, and an imperfect *Alaria*.

#### AGARUM TURNERI, Post. & Rupr.

Ungava Bay. Several rough-dried specimens.

#### CHORDA FILUM, Stackh.

Ungava Bay (Turner, no. 485).

#### DESMARESTIA ACULEATA, Lamour.

Ungava Bay (Turner, no. 507, 535, 4870, and 4872).

#### CHORDARIA FLAGELLIFORMIS, Müll.

Ungava Bay (Turner, no. 500 and 4870), also collected by the Howgate Expedition.

#### RALFSIA DEUSTA, J. G. Ag.

Ungava Bay. A single fine specimen four inches in diameter.

#### DICTYOSIPHON FÆNICULACEUS, Grev.

DICTYOSIPHON FÆNICULACEUS, Grev., var. FLACCIDUS, Aresch.

DICTYOSIPHON HIPPUROIDES, Aresch.?

The species of *Dictyosiphon* are, at the best, difficult of determination, and of the material collected at Ungava Bay it is impossible to speak with certainty, except that some of the few specimens may undoubtedly be named *D. fœniculaceus*. No. 464 is probably the variety *flaccidus*, and no. 475 may be referred with considerable doubt to *D. hippuroides*. Without a larger set of specimens, one could not venture to feel sure of the determination.

#### PHLÆOSPORA TORTILIS, Aresch.

Kikkerton Islands. Growing on small stones, July, 1878. Abundant (Kumlien). This is an interesting addition to our Arctic flora.

The species is said by Kjellman to have been found at Neuherrehut, Greenland. It may be expected to occur in the Gulf of St. Lawrence and perhaps in New England, but it has hitherto escaped the notice of our algologists.

CHÆTOPTERIS PLUMOSA, Kütz.

Kikkerton Islands, July, 1878. "Rarely found on shore, and then mostly on kelp. In nine fathoms, head of Gulf of Cumberland, from a crack in the ice, Feb. 24, 1878." (Kumlien.)

SPHACELARIA ARCTICA, Harv.

Gulf of Cumberland (Kumlien).

ECTOCARPUS LITORALIS, Harv.

All the *Ectocarpus* collected at Ungava Bay, as well as those from the Howgate Expedition, belong to the subgenus *Pylaiella*, and are to be included under Kjellman's *Pyl. litoralis*. Among the Howgate Algæ under the name of *Ect. Farlowii* is a form called var. *robustus* of *Ect. litoralis* in the Marine Algæ of New England, and a specimen in poor condition which may possibly be placed in *Ect. Landsburgii*, Harvey.

CHLOROSPOREÆ.

CLADOPHORA ARCTA, Harv.

Kikkerton Islands, Gulf of Cumberland. "Conspicuously abundant, especially in sandy places." (Kumlien.)

CLADOPHORA GLAUDESCENS, Harv.

Ungava Bay (Turner).

CLADOPHORA GRACILIS, Kütz.?

Ungava Bay. Three specimens, no. 790, 798, and 801, appear to belong to this species, but I am by no means certain.

ULOTHRIX FLACCA, Thuret.

Annanact Harbor (Kumlien).

MONOSTROMA BLYTTII, Wittrock.

Ungava Bay (Turner). A few fine specimens undoubtedly belonging to this species.

## XXVII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF  
HARVARD COLLEGE.ON THE CRYSTALLINE STRUCTURE OF IRON  
METEORITES.

BY OLIVER WHIPPLE HUNTINGTON.

Presented by invitation, May 12, 1886.

THE general octahedral structure of iron meteorites was observed soon after the attention of mineralogists had been directed to this remarkable class of bodies.

In the year 1808, Von Widmanstätten\* of Vienna observed the crystalline figures brought out on a polished section of the Agram iron by tempering or etching, which have since been known by his name. That these figures might be due to an octahedral structure is said to have been remarked by Berzelius,† and as early as 1816 was inferred by Sömmerring from definite measurements of angles between the lines of the figures. In the same year, Wollaston remarked that the iron from Bemdego (Bahia) had an octahedral cleavage,‡ and later, in 1839, still more striking evidences of octahedral structure were described by C. U. Shepard in his paper on the Ashville meteoric iron.§ Furthermore, in 1861 Von Reichenbach studied with great detail all the minute features which are presented by the Widmanstätten figures, and published his results in a series of papers in Poggendorff's *Annalen* entitled "Ueber das innere Gefüge der näheren Bestandtheile des Meteoreisens."|| He first made the distinction between the different conditions of nickeliferous iron forming the material of the crystalline plates of which the Widmanstätten figures are sections, and introduced into the descriptions of these bodies the now familiar terms of *Balkeneisen*,

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\* Schweigger's *Journ.*, Bd. lii. p. 172.† *American Journal*, 8d series, vol. vi. p. 18.‡ *Philos. Trans.* for 1816, p. 281.§ *American Journal of Science*, 1st series, vol. xxxvi. p. 82.|| Poggendorff's *Annalen*, Bd. cxiv.

Bandeisen, and Fülleisen, which he also designated respectively as Kamacite, Taenite, and Plessite.

In the year 1864, Gustav Rose, in his "Beschreibung und Eintheilung der Meteoriten," distinctly pointed out the octahedral arrangement of the plates which form the Widmanstätten figures, and compared the structure of meteoric iron with the lamellar structure of many leucite and magnetite crystals, regarding the crystalline mass as consisting of scales or plates of iron separated by laminæ of the iron and nickel alloy which Reichenbach called Taenite.

In 1848, Neumann,\* in studying the structure of the Hauptmannsdorf (Braunau) iron, concluded that the fine linear markings which appear on etching the faces of the remarkable cubic forms obtained by fracture were essentially distinct from the Widmanstätten figures, and such lines have since been known as Neumann lines, and have been supposed to indicate a cubic structure, just as the Widmanstätten figures had been supposed to mark solely an octahedral structure.

On this basis, iron meteorites are now generally classified under two chief groups, as the octahedral and the cubic. This distinction, originally made by Gustav Rose, has been brought into prominence by Dr. Brezina in his recent catalogue of the collection of meteorites at the Vienna Museum, and in this catalogue both the cubic and octahedral meteorites have been further subdivided by him into numerous sub-groups, marked solely by the width and other features of the figures or lines.

That such a classification cannot be natural or fundamental is shown by the disagreement of equally competent observers in regard to the character of the figures or lines in special cases, and also by the circumstance that the figures may appear very differently on separate masses of the same fall, and even on different parts of the same section. For example, the iron from Ovifack, Greenland, in regard to whose meteoric origin there has been so much question, is described both by Dr. J. Lawrence Smith and Daubrée as yielding distinct well-marked Widmanstätten figures, while Dr. Brezina insists that it shows absolutely none. In like manner, the well-known iron of Santa Catarina is described by Daubrée, Damour, and others, as exhibiting distinct Widmanstätten figures, while Dr. Brezina not only asserts that no figures could be developed on any specimens which have come under his notice, but even calls in question the discrimination of the eminent mineralogist just quoted. Again, Dr. Brezina, in criticising some observations of Dr. Walter Flight of the British

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\* Naturwiss. Abhandlung ber. v. Haidinger, Bd. iii. Abth. ii. p. 45.

Museum, includes the iron of Babb's Mill among those which exhibit no Widmanstätten figures; but the specimens, of unquestionable authenticity, in the collection of Harvard College show well-marked figures. Furthermore, an etched surface on a mass of Nelson County iron weighing 6,800 grammes, and measuring 13 inches in its longest dimension, presents perfectly distinct figures near the centre of the section, which grow indistinct near the edges, and entirely fade out at one end. On the other hand, the iron of La Caille, classed by Dr. Flight with the irons giving no figures, shows, as Dr. Brezina truly remarks, very well developed figures when the sections are made in most directions; but we have etched surfaces of this meteorite which over several square inches of area show no figures whatever.

In view of such differences of observation and opinion as the above examples indicate, it seemed desirable to make a still further study of the crystalline structure of iron meteorites, and Professor Cooke placed at my disposal for this purpose the very large collection of Harvard College, which, since the acquisition of the collection of the late Dr. J. Lawrence Smith, has representatives of all the characteristic meteorites of this class. The writer has been familiar with this collection since it was acquired by the College, and, in examining the specimens from time to time, he has been struck by the indications of crystalline form which many of them present. These appear like rough octahedrons, and their irregular faces present the most striking similarity to cleavage planes, although in some cases the surfaces are covered and the edges rounded by a fused crust. On further examination, it appeared evident that the surfaces in question must be true crystalline faces, for not only were these faces parallel to planes of fracture as indicated by rifts through the mass, but they also stood in a definite relation to the Widmanstätten figures. Moreover, rifts of fracture were common when no external crystalline form could be made out, and hence came the idea of using the cleavage faces as planes of reference in studying the crystalline structure of the iron meteorites; and the plan was formed to grind, polish, and etch surfaces either parallel to the cleavage planes or in a known position towards them, with the hope that it might thus be possible to determine with certainty the relations of the crystalline plates whose cross-sections form the Widmanstätten figures. This was in general the plan of the investigation whose results are here given.

The most striking example of such a rude cleavage form as has been described is a mass of the Franklin County (Kentucky) iron weighing 7,260 grammes, which shows all the planes of an octahedron,

inclined to each other at the regular octahedral angle ( $109^{\circ} 28'$ ) as nearly as the uneven surfaces of the faces would admit of measurement with an application goniometer. This large, unique, isolated octahedron, of massive iron, measures seven inches in its longest dimension, and one of the triangular faces distinctly outlined measures over four inches on each edge. Another face, still more distinctly marked, measures three inches on each edge. At various points there are triangular depressions or reliefs conforming to the general outline, features which are so characteristic of large crystals; and there are also numerous rifts parallel to the octahedral faces. A large part of the surface is covered with a crust, and, on the basis of the usual interpretation of meteoric phenomena, it is obvious that this crystal is the fragment of an iron meteorite broken up after entering the atmosphere, but while still moving rapidly enough to produce a melted crust over the surface of fracture.

Another example in the Harvard collection of external octahedral form is a specimen of the Carthage (Smith Co.) iron. This specimen shows six faces of a rough octahedron, one of the faces having an area of seven square inches. One half of this octahedron has been partially torn apart into numerous smaller crystals, some of them an inch or more in diameter; but though the crevasses between the individuals are in some places nearly a quarter of an inch in breadth, yet they are bound firmly together by a network of plates, which in some parts raggedly jut out from the octahedral faces. The general appearance of the exterior of the specimen reminds one somewhat of a rough mass of galena crystals, only of octahedral form. The rough crystal is evidently the result of fracture, probably caused during the passage of the mass through the air, and the octahedral faces are cleavage planes, if the term cleavage may be applied to such fractures, which cannot be reproduced by splitting in the ordinary way on account of the malleability of the mass. The specimen further exhibits a fused crust over the octahedral faces, which must have formed after the partial breaking up of the large mass, giving a rounded appearance to the edges. On a polished surface, cut nearly parallel to the largest octahedral face, the figures produced by etching appear very strikingly. They are perfectly distinct and regular, being typical Widmanstätten figures; but when they come to the cracked portion of the iron, they appear as separate plates, some having been broken by the rupture, others separated, while the greater number appear bent and strained, but still coherent and binding the mass firmly together. The whole appearance on the etched surface gives at once

the idea of a forcible explosion, and yet all the cracks, even the most ragged, follow directions parallel to the octahedral faces.

A second specimen of the same iron, measuring twelve and a half inches in its longest dimension, and weighing 9,980 grammes, is a very remarkable mass of cleavage octahedrons, loosely packed together and piled on top of each other, not unlike crystals of alum, and almost as sharply defined. The largest octahedral face measures five inches in diameter, but is made up of numerous smaller crystals, in some places jutting out and in others receding, forming numerous triangular projections and depressions.

Another striking octahedral mass is a fragment of the well-known De Kalb County meteorite. One specimen of this iron shows hollow octahedral faces, two inches in diameter, like hopper crystals, consisting of skeletons built up of a series of plates about half an inch wide and one sixteenth of an inch thick. These plates, when cut transversely, constitute the Widmanstätten figures. When the section is cut at random, the figures may differ somewhat in character, and the plates appear to make various angles with each other; but when the etched surface is parallel to an octahedral face, the Widmanstätten figures all make equilateral triangles, their sides being parallel to the octahedral edges.

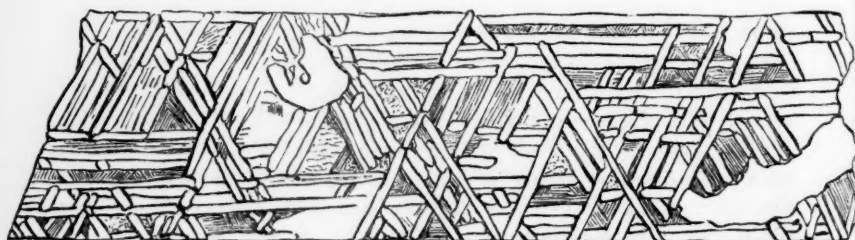


Fig. 1. De Kalb County.

Such a section is shown in Fig. 1, which is part of a surface cut parallel to an octahedral face of the De Kalb specimen just referred to. The figure is an exact sketch, representing the plates of their natural size. The most noticeable character in the figure is the system of broad bands which divide the mass into equilateral triangles. These are cross-sections of the crystal plates, which, in another part of the specimen, stand out so markedly in forming the hollow-faced octahedrons. These plates consist of the purer iron to which Reichenbach gave the name of *Balkeneisen*, or *Kamacite*, and they are

separated from the groundmass by a thin layer of iron rich in nickel, called by Reichenbach *Bandeisen* or *Taenite*. This material is not readily acted upon by acid, and therefore appears on the etched surface as a bright silvery line along the edge of the *kamacite* plates. In some meteorites, as in the *Cocke County* and *Sevier County*, it occurs in sufficient mass to be easily separable from the plates in the form of a thin elastic foil, while in others it almost wholly disappears. The thin plates of "*bandeisen*" resist the action of oxidizing agents, as they resist the action of dilute acid, so that, when the surface of the meteorite becomes disintegrated by air and moisture, these plates not unfrequently become loose, and are easily separated. Dr. Lawrence Smith analyzed the material of some plates thus obtained from the *Sevier County* meteorite, and found in them 27% of nickel. The groundmass consists of what Reichenbach calls *Fülleisen*, or *Plessite*. In the present case, the latter is filled with very thin plates, or "*combs*," in general following the octahedral directions and appearing to be a subsequent crystallization, as if the larger plates had first shot through the mass when in a liquid state, and then, as the interior portions solidified, these also crystallized more or less perfectly, but forming smaller and smaller plates.

Figure 2 shows, double the natural size, one face of a very perfect octahedron broken out from the *Putnam County* meteorite. This

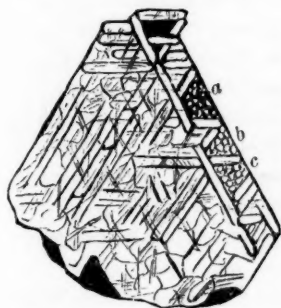


Fig. 2. Putnam Co., Georgia.

iron appears by oxidation of the surface to break up into octahedrons and acute rhombic prisms. The octahedron represented in Fig. 2 was so loose in its structure that it was necessary first to mount it in pitch before grinding the face in order to prevent the plates from splitting off. Here the character is much the same as in the previous one, except that the plates are smaller, and at the points *a*, *b*, and *c* the iron is perfectly granular, showing no signs of crystallization. Moreover, the groundmass,

instead of containing the combs above mentioned, has been broken up by a series of irregular cracks into coarse grains, very much like a mass of crackled glass. Another meteorite which most beautifully illustrates the octahedral arrangement is the *Tazewell* (*Claiborne Co.*) iron, Fig. 3. Here the figures brought out by etching are very sharply defined, but are so small that, in some parts of the field, it

seems as if there were almost no limit to the fine bands as seen with an ordinary pocket lens. The bands, though small, exhibit all the features of the coarser Widmanstätten figures. On the exterior of the mass, small octahedral planes are distinctly visible, and a crack, shown

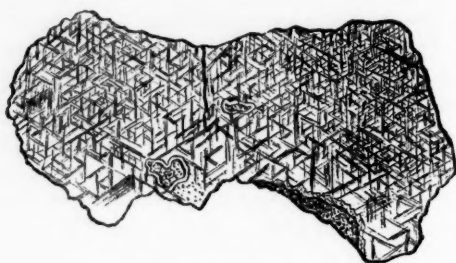


Fig. 3. Tazewell, Claiborne County.\*

by the heavy line in the figure, following the octahedral cleavage, nearly separates the mass into two portions.

So far, the observations on octahedral irons do not differ materially from what has been described in the papers already referred to. The Widmanstätten figures are manifestly the evidence of a very perfect crystallization, chiefly in the octahedral form; and these octahedral plates frequently may be readily separated, the successive depositions of the plates producing a more or less jointed structure, similar to that well known in cap-quartz. But this jointing must be clearly distinguished from the octahedral cleavage or fracture above referred to, which, as already stated, often passes directly through the plates. Moreover, the perfection of the octahedral cleavage does not depend upon the size and character of the Widmanstätten plates, many of the irons which show the best figures affording no evidence of octahedral cleavage, while some of the most compact break readily into octahedrons.

An example of the latter is shown in Fig. 4 from the Butler (Bates Co.) iron, where the larger surface, drawn of its original size, shows that the Widmanstätten figures are very fine, and not in broad, distinct plates, while some of them are even microscopic; and yet

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\* The illustrations of this paper were made by the Lewis Engraving Company, and although in the details they are faithful reproductions of the drawings from which they were taken, yet the lines are all too heavy, and give the idea of a much coarser structure than the meteorites actually present. This is especially true of the above cut.

from this iron was obtained a far more perfect octahedron than from any of those with a coarser structure. The smaller sketch shows one face of such an octahedron, twice the original size. This octahedron showed seven perfectly even regular octahedral faces, the eighth face having been hollowed out where it formed part of the crust of the meteorite.

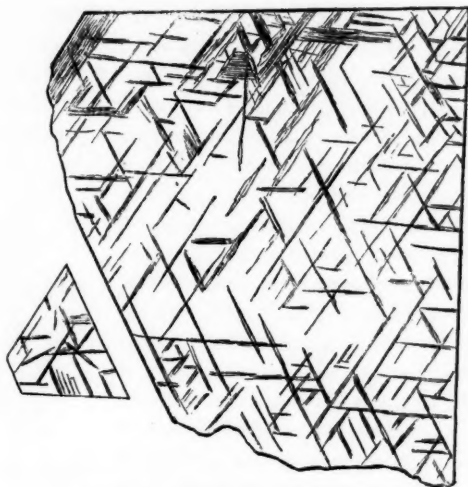


Fig. 4. Butler, Bates County.

All the faces were polished and etched so that the plates might be followed through their entire extent. On examination, it appeared that the majority of the plates, including even the finest microscopic markings, followed the direction of the octahedral faces. But there will be noticed in the sketch of the octahedral face, that, in addition to the usual directions, there appear certain plates which bisect the facial angle of the octahedron. These plates, when followed over an edge on to an adjacent face, were seen to be parallel to an octahedral edge, showing that they must be dodecahedral instead of octahedral.

Thus it at once appeared that the Widmanstätten figures could not be solely characteristic of octahedral structure. Furthermore, the Butler meteorite seemed to stand between well-marked Widmanstätten figures and the finer lines discovered by Neumann and shown by him to be parallel to cube edges. Some of the Butler figures are coarse enough to be classed unquestionably as Widmanstätten, that is, they show the three varieties of iron distinguished by Reichenbach,

which he calls the Trias; while others of the figures are almost microscopic markings, in which distinct plates of kamacite and plessite cannot be made out even under the microscope. Between these two extremes there is every gradation. The Butler meteorite has always been classed among the octahedral irons. We come next to the Coahuila, which has been classed with the so-called cubic irons.

A large section of this iron, on being etched, showed innumerable fine lines, seeming at first sight as irregular as the markings on a chopping-block. When this section was examined under the microscope, it showed all the characters of the Butler figures, only a degree finer. On studying the directions of the lines, they appeared to make every possible angle with each other, but with a prevalence of right angles. The meteorite is very compact, with usually no external crystalline form, but it was found that on one specimen, by quick blows of the hammer, cleavage masses could be broken away. One of these cleavage masses is shown, of twice its original size, in Fig. 5. It has the well-known form of the cube twin, described by Tschermak \* as typical of the Hauptmannsdorf iron, but with this difference, that the cube in this case is modified by the octahedron. On polishing and etching the crystal faces, the lines appeared so fine as to be for the most part indistinguishable by the naked eye, but under the microscope showing most beautiful markings, all parallel either to the cube edges or to those of the octahedron. Most of the lines were so fine as to appear like the finest striations, while a few, on the other hand, were coarse enough to be recognized by a pocket lens as consisting of plates with all the characters of the finer Widmanstätten figures.

In actual contact with the crystal just described appeared an acute rhombic prism with an angle of about  $120^\circ$ . This prism, shown of twice its size in Fig. 6, could only be separated by the hammer over the area  $abcd$ , and the rest of the face had to be continued by cutting through a very compact part of the specimen.  $ab$ ,  $bc$ , and  $cd$  are the natural crystal edges, and the three faces of the prism not shown in the figure were chiefly characterized by the system of fine lines seen here parallel to  $cb$ . The lower of the two drawings was made from the original specimen, without a knowledge of what the

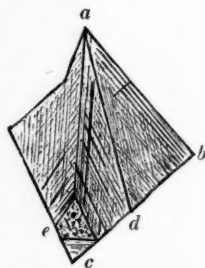


Fig. 5. Coahuila, Mex.

\* Akademie der Wissenschaften Wien, Bd. lxx. Abth. i. p. 449.

angles were; but on examination it was found that the lines, and prism faces as well, could all be referred to a cube with twin members on all the trigonal axes.

The face of such a twin is represented by the diagram between the two figures of the crystal, and the upper figure was actually drawn

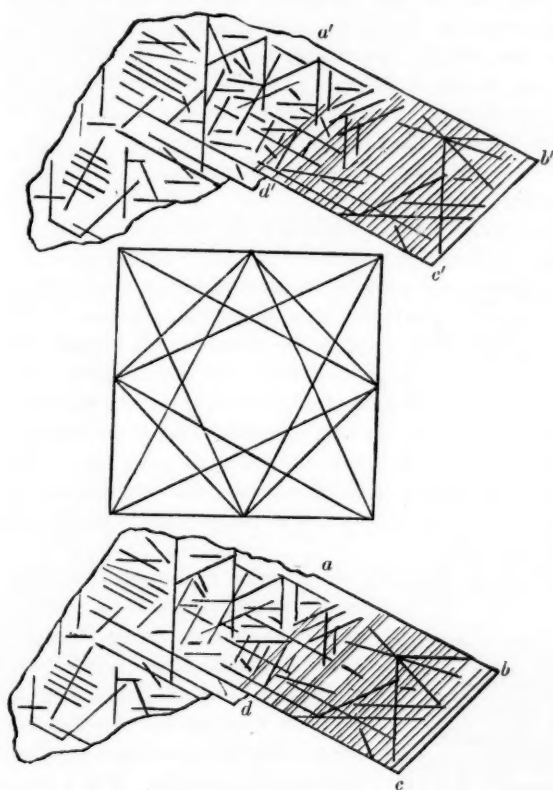


Fig. 6. Coahuila, Mexico.

from the cube diagram by means of a parallel ruler, and it will at once be seen from the close coincidence of the two figures that the upper one must be correct, the lower one only varying within the limit of error of a mechanical drawing.

On examining the Hauptmannsdorf iron, which has long been known to break with a cubic fracture, a cube face under the microscope ap-

peared, as shown in Fig. 7, some of the lines being parallel to the cube edges and others forming diagonals of the cube face. These diagonals might be octahedral lines or dodecahedral lines, or they might be lines of cleavage parallel to the face of the other individual of a twin, and as the face shown in section replacing the cube angle at *a* was the face of a twin cube, the lines parallel to that edge would probably be due to the same plane; and this was proved to be the case, as on an adjacent face the same lines followed the direction of twinning. These lines of twinning are not represented in Fig. 7, to prevent confusion.

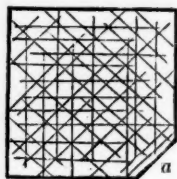


Fig. 7. Hauptmannsdorf (Braunau).

Thus the Hauptmannsdorf iron appears to be purely cubic in structure, while the Tazewell appears to be purely octahedral. However, as the octahedron was observed in the Coahuila iron, and the dodecahedron appeared in the Butler iron, it became a question whether the cube and dodecahedron could not be found in the typical octahedral irons. A very large number of irons were studied with this end in view, but nothing could be determined with specimens where only one face could be examined. It was necessary to have two known crystal faces, and to be able to follow the plates over an edge. For on a cube face the octahedral plates give rectangular intersections, while on an octahedral face the cube plates would give intersections parallel to the octahedral edges.

Figure 8 shows of original size a section of the well-known La Caille

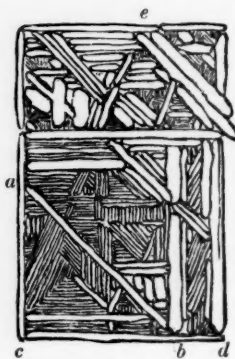


Fig. 8. La Caille.

meteorite, cut parallel to an assumed cube face, the direction being determined by external well-developed octahedral faces. Here the rectangular intersections *ac* and *cd* result from octahedral plates intersecting the cube face, but there are also diagonals of this rectangle. The plate *ab* and those parallel to it make an angle of  $45^\circ$  with *cd*, and when traced on to an adjacent face, cut at right angles to the one in the figure, they follow the direction of a dodecahedral plane, and on the under side of the specimen there appeared a large natural face, an inch in diameter, exactly parallel to this same plate. This face meas-

ured, as shown by an application goniometer,  $145^{\circ}$  with an adjacent octahedral face, showing that it was the face of a dodecahedron truncating the octahedral edge; and when etched neither of these faces showed any Widmanstätten figures, but only a mottled appearance, as is usually the case with a surface consisting of a single plate. The other oblique lines in the direction  $ce$  make an angle of  $66^{\circ} 19'$  with  $cd$ , and are plates of the twin octahedron corresponding to the twin cube before mentioned.

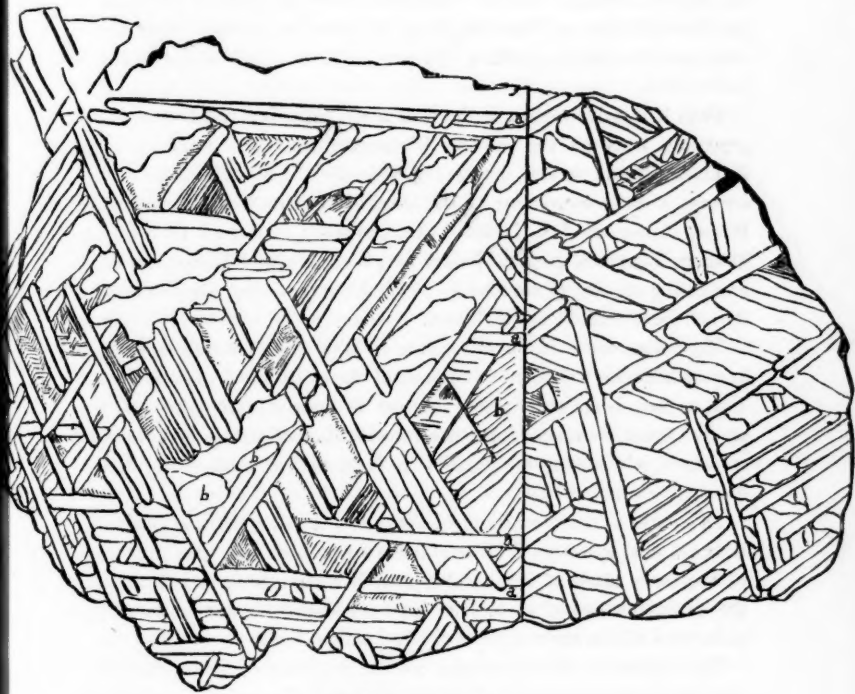


Fig. 9. Robertson County.

Figure 9 shows, of original size, two sections of the Robertson County iron. The left-hand half of the figure is parallel to the octahedral face, while the right-hand half is a face at right angles to the first, and in the upper left-hand corner is shown an octahedral cleavage. Here most of the plates are octahedral, and are at once recognized, but the plates marked  $b$  and also the irregular cloudy-looking masses bisect the octahedral angle, and these follow a dodecahedral direction,

while the plates marked *a* on the octahedral face are parallel to a lateral edge, and, on following the plates on to the face at right angles to the first, it will be seen that they continue to be parallel to the lateral edge. Hence they cannot be octahedral plates, and, since they are parallel to a principal section of the octahedron, they must be cubic. In order to see whether the Robertson County iron was an unusual case of cubic plates, other well-marked Widmanstätten irons were examined and in the same way the cube was found, together with the dodecahedron, in the De Kalb iron before mentioned, and also in the Obernkirchen or Oldenburg iron. Undoubtedly, many other examples could be found, provided the proper faces could be distinguished and etched.

Thus it is evident that, in the first place, there is a regular unbroken gradation between the coarsest Widmanstätten figures and the finest Neumann lines; so that, beginning with the Nelson Co. iron, we can arrange a series consisting of the irons of Wichita Co., Glorietta, Red River, Robertson Co., Dickson Co., Oldham Co., Jewell Hill, Obernkirchen, Tazewell, Butler, Walker Co., Coahuila, and Hauptmannsdorf, presenting regular gradations in which there is no gap where a definite line of demarcation can be drawn.

Moreover, there is no difference in crystalline form even so slight as that between the three fundamental forms of the isometric system. For, as has been shown, the coarsest Widmanstätten figures as well as the finest Neumann lines are intersections of planes of crystalline structure, which may be parallel to faces of the octahedron, the dodecahedron, or the cube.

Of course it is not maintained that there is not a marked distinction between characteristic Widmanstätten figures showing all the features of the three kinds of iron, and typical Neumann lines as exhibited by the Hauptmannsdorf meteorite, but only that both are an outgrowth as it were of the same type of crystallization.

The Germans strongly insist on the divisions of the trias of Reichenbach, and describe the features of kamacite, taenite, and plessite as if they were essentially different substances, instead of merely different conditions of a nickeliferous iron; and the only evidence we have that there is any material difference of composition is based on an analysis cited by Reichenbach\* of the so-called taenite plates, which he had mechanically separated from the Cosby Creek iron, and which were found to contain 13.8 per cent of nickel, while the mass as a whole only contained 9.8; and, on this ground, it is assumed that

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\* Poggendorff's Annalen, Bd. cxiv. p. 258.

kamacite consists of a purer iron. As stated above, Dr. Lawrence Smith found in plates obtained from the Sevier County iron, which is closely allied, if not identical, with the Cosby Creek, 27 per cent of nickel. This supposition would harmonize with our idea of the manner in which crystallization takes place. For though a substance in crystallizing may include foreign substances, still crystallization is a purifying process. Hence, as the molten metal cooled, there would be a tendency for the pure iron to crystallize first, thus forcing back, as it were, a less pure material, which would solidify subsequently; and the natural alternation of such stages, during a very slow process of crystallization, would result in a succession of plates of comparatively pure metal interlaminated with a richer nickel-iron alloy.

This theory is strongly supported by the structure of the Pallasites, where the iron occurs surrounding masses of olivine. Here, as Reichenbach has so beautifully shown,\* the silicate grains are first surrounded by a deposit of kamacite, and the trias does not appear till this layer of the purer iron has been deposited.

Moreover, Tschermak has shown,† in regard to artificial irons, that pure iron tends towards a cubic crystallization with markings similar to the Hauptmansdorf meteorite, while impure iron, like cast-iron, frequently shows imperfect octahedrons and a scaly structure, not unlike that of many meteorites, and this becomes very striking in the so-called Spiegeleisen.

We know as yet very little of the causes which determine the crystallization of substances with an isometric structure in one or another of the three fundamental forms, but we do know that constantly the presence of some foreign material in the crystallizing menstruum produces a marked influence on the result. Thus, common salt, which usually crystallizes in cubes, crystallizes in octahedrons from solutions containing urea. Then again, galena may crystallize under unknown conditions in all three of the fundamental forms. Indeed, the crystallization of galena presents a striking analogy to that of iron as it appears in meteorites. It was shown many years ago, by Professor Cooke,‡ that galena, like the iron, may be cleaved parallel to faces of all three fundamental forms. Usually the cubic cleavage is the most pronounced; but in the remarkable variety from Lebanon County, Pennsylvania, the octahedral cleavage is the more eminent, although both the cubic and dodecahedral can also be easily obtained.

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\* Poggendorff's Annalen, Bd. cxiv. p. 99.

† Akademie der Wissenschaften Wien, Bd. lxx. Abth. i. p. 447.

‡ American Journal of Science, 2d series, vol. xxxv. p. 127.

In connection with this, it is interesting to note that, on polishing and etching octahedral, dodecahedral, and cubic faces on crystals of galena, lines were developed precisely similar in character and position to the Neumann lines. Now it is to be remarked that on the cube faces of the Hauptmannsdorf iron, which Reichenbach regards as consisting of kamacite only, — that is, the purest form of iron, — we have a prevailing cubic structure, as indicated by the so-called Neumann lines. But in proportion as the iron in the process of crystallization has excluded foreign material, as shown by inclusions such as graphite, sulphide of iron (troilite), phosphide of iron (Schreibersite) and the like, the octahedral form prevails.

It is further to be noticed in this connection, that on the sections of kamacite plates in characteristic octahedral irons fine lines appear called "Schraffirungs" by the Germans, which are evidently identical with the Neumann lines, and these follow the direction of the prevailing crystalline form. Hence, on this view, the coarser structure which gives rise to the Widmanstätten figures with the well-marked trias of Reichenbach is connected with the exclusion of incompatible material in the process of crystallization, while the more uniform structure of the so-called cubic meteorites, marked by the Neumann lines, depends on the circumstance that the material was susceptible of crystallization as a whole. It is by no means necessary that, to fulfil this condition, the material should be pure iron. It may be an alloy capable of crystallizing in mass, as is the case with many crystalline alloys.

We conclude, then, that the crystalline structure of the coarsest octahedral irons is not more definite than that of the cubic irons; but in the first case the process of crystallization determines the elimination of the various materials which form the Widmanstätten plates, while in the second case no such elimination takes place, and between these extremes there is every gradation. The element of time may also be an important, and perhaps the chief, condition in determining the result, for we should naturally expect that, during a very slow crystallization, foreign material would be more completely eliminated than during a process which was comparatively rapid. That the crystalline structure is equally definite in both cases, is shown by the fact that cleavage forms may be developed with equal readiness in either class of irons.

Though there are no very definite data in regard to the crystallization of nickeliferous alloys, yet it has been suggested that the presence of nickel in the meteoric iron might determine its crystalliza-

tion. It has been thought that between certain limits in the per cent of nickel present octahedral structure might result, while with a different amount of nickel the crystallization would be cubic. With an idea of determining this point if possible, the analyses of eighty meteoric irons, as given in various scientific journals, were tabulated according to their per cent of nickel, and at the same time the size and character of the figures produced by etching were noted. Unfortunately, these results appeared so discordant that no trustworthy conclusion could be drawn from them, for it was frequently the case that the composition of the same meteorite as given by equally competent analysts differed by several per cent. Thus the per cent of nickel in the Babb's Mill meteorite has been variously stated as 14.7, 17.1, 4.7, and 12.4, and yet this appears to be a perfectly homogeneous iron.

Dr. Flight of the British Museum has made the remark, that Widmanstätten figures seldom appear in irons containing more than nine per cent of nickel, and it seems to be true that most of the irons giving well-marked Widmanstätten figures contain from five to nine per cent of nickel, though they vary all the way from 3.12 to 17.37 per cent. On the other hand, the irons giving well-marked Neumann lines contain generally only five or six per cent of nickel, but the data at present are insufficient to afford any basis for generalization.

Moreover, it is by no means as yet established that the amount of nickel present is the cause which determines the difference of feature in the crystallization of meteoric irons, nor should we be led to infer that such would be the case from the behavior of alloys of metals so closely allied as nickel and iron. It is certainly quite as probable that the effect may be due to some other impurity, — for example, to the presence of phosphorus, which is known to produce such marked effects on the physical properties of iron. According to the analysis of Reichenbach already cited, the taenite plates of the Cosby Creek meteorite contain 0.295 per cent of phosphorus, while the mass only contains 0.089 per cent, and it is well known that Schreibersite, which is a phosphuret of iron containing fourteen per cent of phosphorus, constantly appears on sections of meteoric iron, in lines along the bands of kamacite. But our knowledge of the amount of phosphorus in the different meteorites is even less complete than our knowledge of the per cent of nickel. We do not know, in regard to any of the impurities, either the average amount in any considerable portion of the meteoric mass, or to what extent the amount varies in different

portions of the same mass. The most we know, in any case, is the composition of one or more fragments selected for analysis, and, as we have shown, even these data are so discordant as to be wholly untrustworthy. It is impossible to infer with certainty from the descriptions whether the disagreement arises from faulty methods of analysis, or from actual difference of composition in the fragments selected, and no satisfactory conclusions can be reached in regard to the influence of impurities on the crystalline structure, until an extended series of systematic analyses has been made of the iron meteorites, by processes which have been well considered, and the limits of whose accuracy have been carefully determined. In such a chemical investigation, regard should be paid to the probable variation in composition of different parts of the mass. This is a subject to which we hope to return at a future time.

The action of the process of crystallization in eliminating impurities produces effects with many minerals not unlike those of the Widmanstätten figures. Very striking exhibitions of such effects may be seen with the microscope in rock-sections containing crystals of leucite, nosean, nepheline, and other minerals. Illustrations of these phenomena have been given in works on lithology, and it is only necessary to allude to them here, in order to make clear their analogy with the phenomena we are studying. But a far more striking illustration of this similarity is shown by a large specimen of fluorite in the Harvard collection, which has been cut through a mass of compacted crystals. The polished surface imitates very closely the features of the Widmanstätten figures. There are distinct bands, marked by difference of color instead of difference of lustre, separated from the groundmass of the mineral by definite layers of less pure material. The bands are about the width of those in the Glorietta meteorite, and they all appear alike, bordered in every case by the same layers of impurities arranged in a definite order, and these bands, crossing at various angles, with a predominance of right angles, bear a most striking resemblance to the Widmanstätten figures. Such examples as these indicate clearly that the Widmanstätten figures are not a peculiar phenomenon, but that such an alternation of plates is often a characteristic of crystalline structure, when the process of crystallization is attended by the elimination of foreign material.

There is another feature of the Widmanstätten figures which often appears, and which is best explained by the assumption that the process of crystallization was extremely slow. Figure 10 shows two

faces of a very perfect octahedron, drawn of original size, from the Cranberry Plains (Poplar Camp) iron. It will be seen by this sketch that the octahedral outline has been sharply formed; but while



Fig. 10. Cranberry Plains.

many of the Widmanstätten plates are parallel to this outline, there are others which are markedly curved. These curved plates must have originally formed through the liquid mass as true planes, like their neighbors, and have been bent in the subsequent solidifying of the remaining material. For, if they had been distorted by

an exterior force, the regularity of the octahedron would have been at the same time destroyed.

This phenomenon of curved plates has been made a basis of subdivision in the classification of iron meteorites. But it is evident from the figure that the bending is not a constant or essential character, as the plates are not all curved, but only appear so at particular parts of the mass, and some specimens show no trace of such a feature. In a word, such curved plates are simply accidents of the crystallization. Very similar bending is common in various minerals, as in gypsum, and very conspicuously in the beautiful crystals of stibnite which within the few last years have been brought from Japan.

A similar remark might be made in regard to the swellings formed in the kamacite plates around inclusions of troilite, Schreibersite, and the like, which have been so minutely described by Reichenbach, and named by him "Wülsteisen."\* These again are accidents of crystallization, which have their counterpart in other crystals, and are most beautifully shown on the plates of mica from Chandler's Hollow, Delaware, where the depositions of magnetic oxide of iron on the planes of the crystalline growth of the mica produce effects which imitate in a most striking manner the Widmanstätten figures.

We give in Fig. 11 as perfect a representation of one of these mica plates as could be obtained by the photographic process used in illustrating this paper, and it will be seen that the resemblance is very close. The analogy here is far more than superficial, and shows, as we conceive, the mode of action by which the Widmanstätten figures were produced. This will be evident if it is borne in mind that the figures on the mica plate are also sections of planes of crystalline growth on which the particles of oxide of iron eliminated during the

\* Poggendorff's *Annalen*, 1861, Bd. cxiv. p. 477.

process were deposited. Of course, the mere resemblance in the outline of the two sets of figures is accidental, and arises from the circumstance that the planes of crystalline growth of muscovite mica are

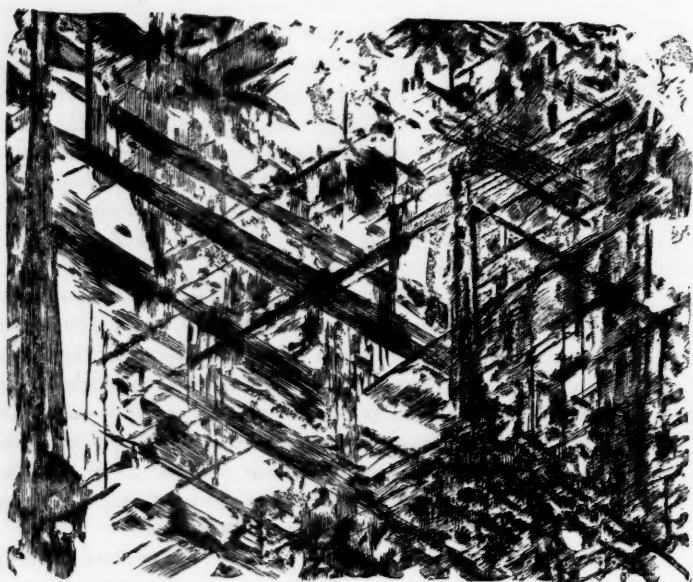


Fig. 11. Mica, Chandler's Hollow, Delaware.

parallel to a rhombic prism of sixty and one hundred and twenty degree angles, the right section of such a prism being similar to the section of a regular octahedron parallel to one of its faces.

The conditions of the plessite which fills the cavities between the crystalline plates of iron meteorites also present features which are especially characteristic of the crystallization of alloys. Sometimes the space is packed with small crystalline plates parallel to those of the external form, the combs already mentioned, shown in Fig. 1. Again the material is granular, as shown at *a*, *b*, and *c*, Fig. 2, or again divided into polygonal masses as shown in the same figure. Similar features in the alloys of zinc and antimony have been described by Professor Cooke,\* and in the alloys of copper and zinc by Prof. F. H. Storer.† They correspond to that pasty condition

\* *Memoirs of the American Academy, New Series*, vol. v. pp. 336-371.

† *Ibid.*, vol. viii. pp. 27-56.

so well known to plumbers and workers in alloys. We here refer only to the conditions of the plessite; but at times we also find the whole meteoric mass divided up by small cracks, and thus rendered so friable that it can readily be broken into coarse polygonal grains with a hammer. Such a disintegration must have been a mechanical one, affecting the whole mass subsequent to its solidification. It is similar to the well-known effects produced on iron by long-continued jarring, and may have been the result of the violent concussions which are known to be caused by the passage of the meteorite through the air. We have recently had the opportunity of examining a specimen of aluminum bronze sent to the Laboratory of Harvard College by Prof. C. F. Mabery of Cleveland, Ohio, which most strikingly illustrates the effect here described. The bronze, consisting of 90% copper and 10% aluminum, had been cast into a bar and reheated for forging. When the heated bar was laid on an anvil and struck with a hammer, it broke up into small polygonal grains, just like those of the Cosby's Creek and Seelasgen meteorites.

Such products as have been described all point to a very slow cooling of the molten metal out of which the crystals came, and this is the opinion held by the best observers in regard to this process. Thus Mr. Sorby writes: "These facts clearly indicate that the Widmanstätten's figuring is the result of such a complete separation of the constituents, and perfect crystallization, as can occur only when the process takes place slowly and gradually. They appear to me to show that meteoric iron was kept for a long time at a heat just below the point of fusion, and that we should be by no means justified in concluding that it was not previously melted. Similar principles are applicable in the case of the iron masses found in Disco; and it by no means follows that they are meteoric, because they show the Widmanstätten's figuring. Difference in the rate of cooling would serve very well to explain the difference in the structure of some meteoric irons, which do not differ in chemical composition; but as far as the general structure is concerned, I think that we are quite at liberty to conclude that all may have been melted, if this will better explain other phenomena."\* Similar opinions have been expressed by Tschermak and Haidinger.

We have tried in this paper to establish the following points:—

First. That many of the masses of meteoric iron in our collec-

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\* *Nature*, 1877, vol. xv. p. 498.

tions are cleavage crystals, broken off probably by the impact of the mass against the atmosphere.

Secondly. That these masses show cleavages parallel to the planes of all the three fundamental forms of the isometric or regular system, namely, the octahedron, the cube, and the dodecahedron.

Thirdly. That the Widmanstätten figures and Neumann lines are sections of planes of crystalline growth parallel to the same three fundamental forms of the isometric system.

Fourthly. That on different sections of meteorites Widmanstätten figures and Neumann lines can be exhibited in every gradation, from the broadest bands to the finest markings, with no break where a natural line of division can be drawn.

Fifthly. That the features of the Widmanstätten figures are due to the eliminations of incompatible material during the process of crystallization.

This investigation throws no new light upon the origin of meteorites, except so far as it strengthens the opinion that the process of crystallization must have been extremely slow. The occurrence of large masses of native iron occluding hydrogen gas, and containing nickel, cobalt, phosphorus, sulphur, etc., implies a combination of conditions which the spectroscope indicates as actually realized in our own sun and in other suns among the fixed stars, and the most probable theory seems to be that these masses were thrown off from such a sun, and that they very slowly cooled, while revolving in a zone of intense heat.

In this paper we have not taken into consideration a number of iron masses, whose meteoric origin has been generally accepted, which show no Widmanstätten figures and not even any Neumann lines. A considerable proportion of these are certainly not meteoric. In the Harvard cabinet there are two specimens, labelled respectively Campbell County, Tennessee, and Hominy Creek, North Carolina, which are evidently nothing but cast-iron, and a third, labelled Tarapaca Hemalga, Chili, which is probably of similar material. We could find on the specimens of this class in the Harvard collection no distinct evidences of crystallization; but also we could find no features incompatible with that unity of structure which it has been the chief object of this paper to illustrate.

## XXVIII.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XXV.—NOTES ON EQUAL TEMPERAMENT AND THE  
CHARACTER OF MUSICAL KEYS.

BY CHARLES R. CROSS.

Communicated February 16, 1886.

THE question as to how closely the tuner of a keyed instrument actually realizes the isotonic scale upon the instrument is one of much interest, regarding which there has hitherto been but little information accessible. Some very recent and valuable results of measurement will, however, be found on page 485 of the new edition of Mr. Ellis's translation of Helmholtz's *Tonempfindungen*, which should be compared with those which are given farther on in this paper.

The following measurements were made by Mr. William T. Miller and myself several years since, but have not been published hitherto, in the hope that they might be extended further, and to additional instruments. But this has not thus far proved feasible.

The best available instrument upon which to make such experiments appeared to be a good cabinet organ, and therefore a freshly tuned single-reed cabinet organ, made by Messrs. Mason and Hamlin, was hired of them for the purpose. The instrument was not tuned especially for us, however, but taken at random from the ware-rooms. The tonometer used was made by Koenig, and consisted of a set of thirteen forks tuned carefully to the isotonic scale, running from middle C, of 269.2 vibrations per second, to the octave of this. These forks, according to the maker, were correct within less than one tenth of a vibration. The notes of the cabinet organ throughout the octave, from  $C_3$  to  $C_4$ , were carefully compared by the method of beats with the corresponding forks. The temperature varied but little from  $78^\circ$  F. during the experiments.

As considerable change in the rate of the reeds could be made by varying the strength of the air-pressure from the bellows, care was

taken to avoid such variation as far as possible. It was found possible to reduce this to a very small amount, by always keeping the bellows full by gently and continually moving the feet. The same result could also be secured by filling the bellows full of air, and then allowing the pressure to diminish gradually, not forcing in air while the beats were being counted. This sufficed, however, only when the duration of the sound was brief.

In counting the beats we were usually able to count either ten or twenty in a series, and six or eight series were taken in succession before passing to the following note. The extreme difference in the duration of a series of ten or twenty beats was very rarely over five tenths of a second, and generally was less than this. The times were estimated by means of a stop-watch reading to eighths of a second.

Three complete and separate sets of comparisons were made at different dates between all the forks and the corresponding reeds of the cabinet organ. The rate of the highest note measured — that is,  $C_4$ , an octave above middle C — was in each case taken as that on which to construct the calculated scale, as experiment showed that the beats were better defined in the upper portions of the scale. The calculated vibration periods of the isotonic scale thus determined were compared with the periods of each one of the notes comprised in that scale as given by the organ, and the differences noted. The organ had, of course, been tuned from a C fork.

The following table gives the difference between the observed and calculated values of each note, assuming in each case, as just stated, that the scale was based on the high C. The differences are called positive when the observed value is the greater.

Name of Note.	Series A.	Series B.	Series C.
C	0.1	-0.1	0.4
$C\sharp$	0.1	-0.1	0.3
D	0.1	0.0	0.3
$D\sharp$	-0.7	-0.7	-0.4
E	-0.5	-0.1	0.0
F	-0.2	-0.1	0.1
$F\sharp$	-0.8	-0.5	-0.3
G	-0.2	-0.5	0.0
$G\sharp$	-0.8	-0.1	-0.7
A	-0.6	-0.5	-0.3
$A\sharp$	-0.7	-0.6	-0.2
B	-0.3	-0.4	-0.2
C	0.0	0.0	0.0

It appears from these figures that in no case is there a deviation of as much as one vibration per second in the scale as given by the organ from the true isotonic scale. It will also be observed that in each of the three series the errors in the upper portion of the scale are all negative, though this is probably accidental. The instrument was presumably tuned from a fork of approximately 536 vibrations per second.

There is a certain interest attaching to the foregoing measurements from their bearing on the origin and nature of the musical characteristics of different keys. It has always been difficult to account for the existence of such differences upon an equally-tempered instrument; and a favorite way of explaining it has been to suppose that the actual scale is not really an isotonic one, but that the scale of the tuner, as carried in his mind and secured on the instrument, is such as to give values to different notes that will really preserve their characteristics to the various keys. It is hard to understand how this can be the case when one considers the methods used by a tuner; and our own results, as do also those of Mr. Ellis, lead to the conclusion that the impression in question is an incorrect one. What is true of the cabinet organ and piano must also be true of other keyed instruments, as any noteworthy differences between instruments professing to be tuned to the same isotonic scale would immediately be noticed.

Helmholtz suggests that with stringed instruments differences of key may arise from the use of open or closed strings, or closed strings of different lengths, and, while denying the existence of such key-differences upon the organ, admits them to exist with the piano, and considers that they are there produced by difference of fingering, according to the position on the keyboard of the keys struck.

In order to test this, the following experiment was tried. Three pianos were taken, all of the same make and pattern, and of as nearly the same quality and loudness of tone as possible. The three instruments were originally at the same pitch. One of them was raised in pitch throughout the whole scale by half of an isotonic semitone, and a second was lowered by the same amount, while the third remained unaltered as a standard of comparison. Hence, the pianos of highest and lowest pitch were a semitone apart; that is, the scale was, so to speak, shifted upward by one key in one instrument with reference to the other. Hence, chords played upon the same notes of the keyboard would be of different pitch, although in the same musical key. On the other hand, chords composed of notes of exactly the same absolute pitch in the different instruments would be in different mu-

sical keys, since sounded by different groups of keys on the keyboard. Now, if there is any characteristic difference of key under these circumstances due to fingering, as Helmholtz supposes, it should be possible to detect a difference of this nature according to which one of the two pianos the chords were sounded upon, these chords being of identical pitch in both. But neither in detached nor successive chords could we observe any difference whereby we could determine on which of the pianos these were played, provided the eyes were closed. There was a slight difference in quality of tone, which sometimes revealed the instrument, even when but a single key was struck; but nothing beyond this. We were confirmed in our judgment by that of several musicians, who were afterwards invited to listen to the instruments. It would be interesting, however, to repeat the experiment, and obtain the opinions of a large number of musical experts.

The measurements cited go to show that any differences in key which exist on instruments tuned to the isotonic scale by a good tuner cannot be due to instinctive deviations from the mathematically perfect scale, whereby the alleged characteristic peculiarities of the different keys are preserved. And our experiments with the pianos seem to indicate that key-differences are not in this instrument caused by differences in fingering; and, indeed, that any differences independent of pitch do not exist at all. Moreover, I doubt very much if the character of any harmony is changed in passing from a piano to an organ, and am inclined to believe that harmonies upon an organ give the same impression, so far as their key is concerned, as when played upon a piano, although, as Helmholtz remarks, in the case of the organ there can be no key-differences caused by differences in fingering. Still further, one can hardly see why the same characteristics of each key should be found on instruments of the violin and piano families, and on reeds and brass as well, if they owe their origin in each case to peculiarities inherent in the manner of playing each class of instrument.

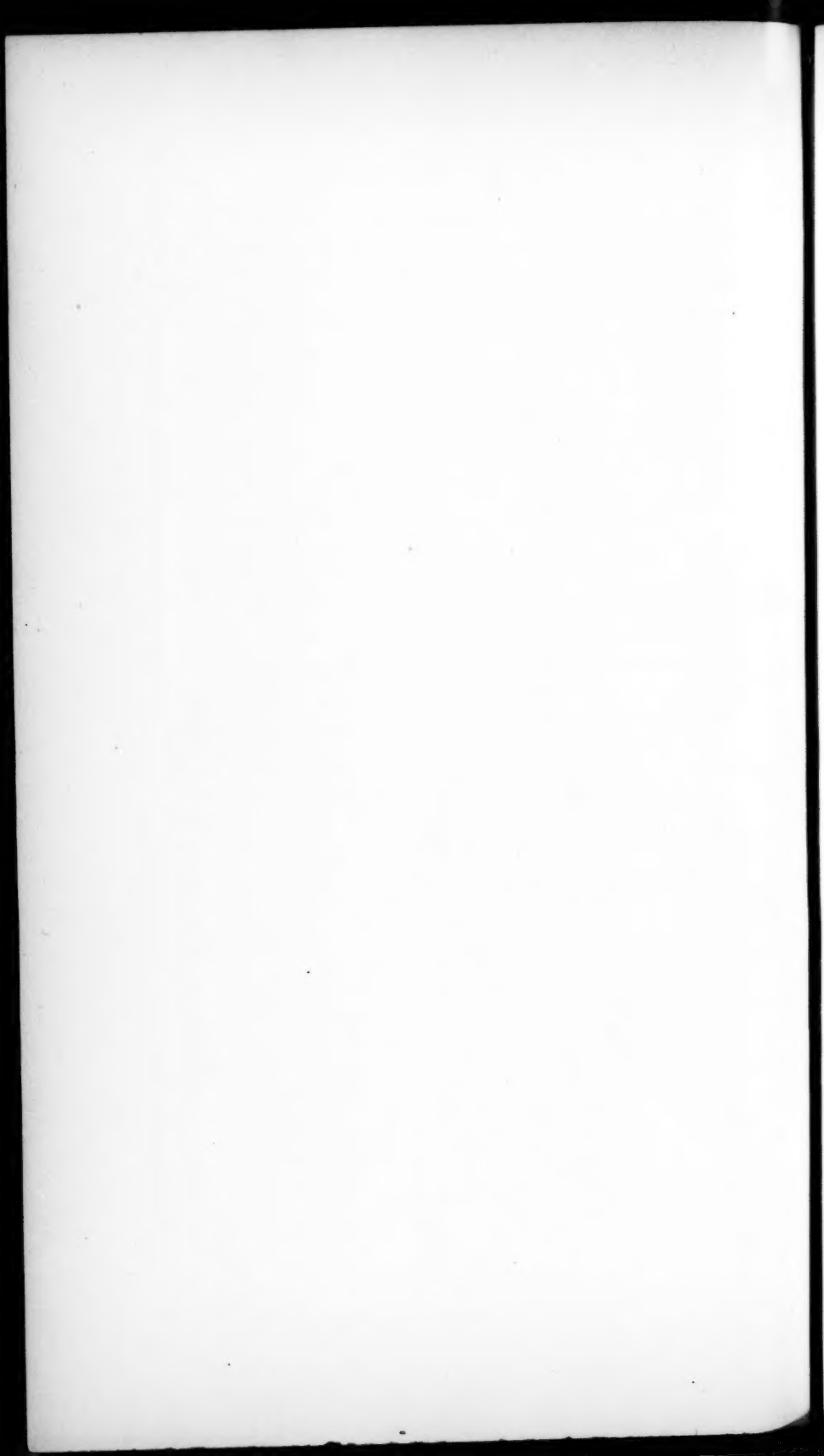
I can speak but very diffidently upon a subject which is so largely one only to be appreciated and discussed by a musician; but to me it seems extremely probable that there is no absolute character pertaining to any key. We notice the pitch of various passages, and, so far as we are habituated to any particular pitch, become accustomed to hear the notes of certain chords at that pitch, and so, on account of the peculiar character possessed by a group of notes having those particular pitches, we assign that character to the key to which the chord belongs. If the notes composing the chord are changed in absolute,

but not in relative pitch, the change in the absolute pitch of the notes constituting the chord of the same name is noticed, and the changed effect attributed to some characteristic of the new key. And if, with a harmony which we have been accustomed to hear performed with all its notes at a tolerably definite standard pitch, the pitch of each note is changed by the same interval, and by an amount as great, for example, as a semitone, so that we realize the transposition, the harmony will seem to have a different character, which we attribute to its being in a different key.

I question very greatly if the impression which any of the instrumental music of Handel, Bach, or Mozart produces upon us, when played at the highest recent concert pitch, a markedly different effect from that which was produced when the low pitch at which those masters wrote was in vogue. Of course, merely noticing a change in character, which we may attribute to change in key, when the pitch is intentionally lowered a semitone, would prove nothing, as any ear keen enough to notice the change would carry the recollection of the high pitch at which it had usually been heard.

In view of the fact that music of the most varied characteristics has been written in the same keys, it is hard to understand how any such inherent character as is popularly imagined can attach to them. It seems much more likely that the great success of some eminent composer in writing music of a particular kind in a certain key has tended to stamp that character upon that key, in the minds of musicians; and later composers may even have been led to choose such a key from its imagined superiority for their purposes.

ROGERS LABORATORY OF PHYSICS,  
February, 1886.



## PROCEEDINGS.

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Seven hundred and eighty-third Meeting.

May 26, 1885. — ANNUAL MEETING.

The PRESIDENT in the chair.

The Corresponding Secretary presented the Report of the Council.

The following gentlemen were elected members of the Academy: —

John Codman Ropes, of Boston, to be a Resident Fellow in Class III., Section 3.

Ezekiel Gilman Robinson, of Providence, to be an Associate Fellow in Class III., Section 1.

The annual election resulted in the choice of the following officers: —

JOSEPH LOVERING, *President.*

OLIVER W. HOLMES, *Vice-President.*

JOSIAH P. COOKE, *Corresponding Secretary.*

WILLIAM WATSON, *Recording Secretary.*

HENRY P. KIDDER, *Treasurer.*

NATHANIEL D. C. HODGES, *Librarian.*

### *Council.*

AMOS E. DOLBEAR,  
ROBERT H. RICHARDS, } of Class I.  
WOLCOTT GIBBS,

ALEXANDER AGASSIZ,  
 BENJAMIN E. COTTING, } of Class II.  
 SERENO WATSON,

JAMES B. AMES,  
 JUSTIN WINSOR, } of Class III.  
 ANDREW P. PEABODY,

*Rumford Committee.*

WOLCOTT GIBBS, JOSIAH P. COOKE,  
 EDWARD C. PICKERING, JOSEPH LOVERING,  
 JOHN TROWBRIDGE, GEORGE B. CLARK,  
 ERASMUS D. LEAVITT, JR.

*Member of the Committee of Finance.*

THOMAS T. BOUVÉ.

The President appointed the following standing committees:—

*Committee of Publication.*

JOSIAH P. COOKE, ALEXANDER AGASSIZ,  
 WILLIAM R. NICHOLS.

*Committee on the Library.*

HENRY P. BOWDITCH, HENRY W. HAYNES,  
 BENJAMIN A. GOULD.

*Auditing Committee.*

HENRY G. DENNY, AUGUSTUS LOWELL.

The following appropriations were voted:—

For general expenses . . . . .	\$2,200
For publications . . . . .	2,000
For the library . . . . .	1,000

Professor Pickering called attention to the urgent need of a complete index to all the publications of the Academy, and, on his motion, it was

*Voted*, To refer this matter to the Committee of Publication.

On the motion of the Corresponding Secretary, it was

*Voted*, To meet, on adjournment, on the second Wednesday in June.

The following papers were presented by title : —

Contributions from the Physical Laboratory of Harvard University. — I. On a New Method of determining the Mechanical Equivalent of Heat. By A. G. Webster.

Researches conducted with the Aid of the Rumford Fund. I. Early Experiments in transmitting Musical Sounds. II. Observations of Atmospheric Refraction. III. Accidental Errors and the Rejection of Doubtful Observations. IV. Stellar Photography. V. Specular and Diffuse Refraction and Reflection. By Edward C. Pickering.

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Seven hundred and eighty-fourth Meeting.

JUNE 10, 1885. — ADJOURNED ANNUAL MEETING.

The PRESIDENT in the chair.

The President announced the death of the oldest Resident Fellow, Robert Treat Paine, of Brookline.

The Corresponding Secretary read a letter from Mr. John C. Ropes, acknowledging his election as a Resident Fellow.

The report of the Treasurer was received and audited.

The report of the Librarian was read and accepted.

The following report of the Rumford Committee was read and accepted : —

The Rumford Committee present the following report for the year ending with this Annual Meeting.

The researches connected with light or heat which have been instituted or continued from last year, and conducted by sub-committees of the general Committee, are, —

1st. On some Applications of Spectrometry and Photometry to Astronomy. By Prof. E. C. Pickering.

2d. On a Standard of Light. By Prof. Trowbridge.

3d. On the Effect of Extreme Temperatures on the Strength of Magnets. By Prof. Trowbridge.

4th. On the Electrical Control of Equal Temperature, &c. By Prof. W. A. Rogers.

5th. On Dry-Plate Photography. By Mr. W. H. Pickering.

The results which have been reached in these researches have been communicated to the Academy during the year, and will appear in fuller detail in the forthcoming volume of Proceedings.

The Academy appropriated for the use of the Rumford Committee \$1,000. Of this sum only \$431.16 has been paid out by the Treasurer.

In this, as in former years, the income of the Rumford Fund has also been useful in relieving the general fund. It contributed \$428.18 towards the payment of the printing of Vol. XIX. of Proceedings, and \$142.64 for the purchase of books or journals relating to light or heat.

In conclusion, the Rumford Committee recommend an appropriation of \$1,000, to be expended for researches on light or heat, with the understanding that the unexpended balance of last year, viz. \$568.84, remains in the hands of the Treasurer.

All which is respectfully submitted,

JOSEPH LOVERING, *Chairman.*

Boston, June 10, 1885.

In accordance with the recommendation of the Rumford Committee, it was

*Voted*, To appropriate the sum of one thousand dollars (\$1,000) from the income of the Rumford Fund to be expended for researches on light or heat.

The following paper was presented:—

On the Influence of Magnetic Stress upon the Capacity of an Electric Condenser. By Alonzo S. Kimball.

The following papers were presented by title:—

Photography of the Corona without an Eclipse. By William H. Pickering.

Contributions to the Botany of North America. By Asa Gray.

Comparison of Alcohol Thermometers Baudin 8208 and 8209 with the Air Thermometer at Low Temperatures. By Anthony C. White.

Determination of the Orbit of Comet 1883. I. (Brooks) from three Normal Places comprising 41 Observations. By Oliver C. Wendell.

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Seven hundred and eighty-fifth Meeting.

October 14, 1885.—STATED MEETING.

The PRESIDENT in the chair.

The President announced the death of Henri Milne Edwards, Foreign Honorary Member.

The Corresponding Secretary read the following letters: from H. Wild, acknowledging his election as Foreign Honorary Member; from the Royal Society of Northern Antiquaries, announcing the death of its Vice-President, M. Worsaae; from Lieutenant Charles R. Miles, Secretary of the United States Naval Institute at Annapolis, inviting the members of the Academy to be present at the reading of Lieutenant Danenhower's paper on the polar question.

The following gentlemen were elected members of the Academy:—

Edward Singleton Holden, of Madison, Wisconsin, to be an Associate Fellow in Class I., Section 2.

George Washington Cullum, of New York, to be an Associate Fellow in Class I., Section 4.

George Shattuck Morison, of New York, to be an Associate Fellow in Class I., Section 4.

The following papers were presented:—

On the Apparent Position of the Zodiacal Light. By Arthur Searle.

The Measurement of the Strength of Telephone Currents. By Charles R. Cross and James Page.

The Thermal Telephone. By Charles R. Cross.

On the Square-Bar Micrometer. By Seth C. Chandler, Jr. (By title.)

Professor Dolbear spoke of the philosophical structure of the magnet, and exhibited a magnet made of brass upon which iron had been deposited by the action of a galvanic current.

Professor Searle read a paper by William A. Rogers, entitled, "Observations on the Flood Rock Explosion."

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Seven hundred and eighty-sixth Meeting.

November 11, 1885. — MONTHLY MEETING.

The PRESIDENT in the chair.

The Corresponding Secretary read letters from Messrs. Cullum and Morison, acknowledging their election into the Academy.

The President announced the death of Dr. William B. Carpenter, recently nominated for Foreign Honorary Membership.

Professor Marquand exhibited and explained the operation of a new logic machine invented by himself.

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Seven hundred and eighty-seventh Meeting.

December 9, 1885. — MONTHLY MEETING.

The PRESIDENT in the chair.

The following papers were presented: —

Experiments upon the Determination of the Temperature of Metals as a Function of their Mass. By William A. Rogers and Austin L. McRae.

On Atmospheric Refraction. By Edward C. Pickering.

Mr. Whiting showed experimentally a new method of determining the rate of vibration of a tuning-fork.

Mr. Chandler called the attention of the Academy to an error in the formula relative to the ring micrometer. This error had been repeated in several editions of Bruno's Spherical Astronomy.

## Seven hundred and eighty-eighth Meeting.

January 13, 1886. — STATED MEETING.

The PRESIDENT in the chair.

The Corresponding Secretary made a short report on the preparation of a complete index to the publications of the Academy. This report was, after a brief discussion, referred back and the committee continued.

The Corresponding Secretary was requested to communicate to the family of the late Dr. Carpenter the fact of his nomination, and to express their grief on his death, which prevented his election at this meeting as Foreign Honorary Member of the Academy.

The following gentlemen were elected members of the Academy:—

Gaetano Lanza, of Boston, to be a Resident Fellow in Class I., Section 4.

William Thompson Sedgwick, of Boston, to be a Resident Fellow in Class II., Section 3.

Pierre Joseph van Beneden, of Louvain, to be a Foreign Honorary Member in Class II., Section 3, in place of the late Carl Theodor Ernst von Siebold.

Felix Joseph Henri de Lacaze-Duthiers, of Paris, to be a Foreign Honorary Member in Class II., Section 3, in place of the late Henri Milne Edwards.

The following papers were presented:—

Biographical notice of the late Dr. Samuel Cabot. By Oliver W. Holmes.

On the Capitalization of Land in Early Society. By Denman W. Ross.

On the Coincidence of Certain Lines in the Stellar, Solar, and Electric Arc Spectra. By William H. Pickering.

Mr. Whiting presented a note on a method of determining simple rigidity by vibration under torsion.

Seven hundred and eighty-ninth Meeting.

February 10, 1886. — MONTHLY MEETING.

The PRESIDENT in the chair.

Communications were read by the Corresponding Secretary from H. M. Hugunin, of Chicago, relative to changing the date of the beginning of the civil year; from the Royal Society of New South Wales, enclosing a list of original researches for which the society offered prizes; from the President of the Society of Physics and Natural History at Geneva, announcing the subject of the De Candolle prize; from the French-Canadian Institute at Ottawa, giving a history of the foundation of the institution, and soliciting funds for its maintenance; from Commodore George E. Belknap, Superintendent of the United States Naval Observatory, communicating a programme of the work to be pursued at the Observatory during the current year.

The President announced the death of Henry P. Kidder, Treasurer of the Academy.

The following papers were presented:—

Thunder-storms in New England in 1885. By William M. Davis.

Observations of Variable Stars in 1885. By Edward C. Pickering.

Professor Pickering exhibited photographs illustrating the application of photography to transit observations. He also described a method by which the entire aperture of any telescope might be used for photographing stellar spectra without employing a slit.

Professor Hooper read a paper by Professor Dolbear on the conditions that determine the length of the spectrum.

The Corresponding Secretary presented, by title, the following papers:—

On Benzotrisulphonic Acid. By C. Loring Jackson and John F. Wing.

On the Action of Sodium on Tribenzylamine. By C. Loring Jackson and John F. Wing.

## Seven hundred and ninetyeth Meeting.

March 10, 1886. — STATED MEETING.

The PRESIDENT in the chair.

The President announced the death of Professor William Smith Clark, of Amherst, Resident Fellow.

The Corresponding Secretary read letters from Mrs. Carpenter, thanking the Academy for the intended honor to her late husband; from the Society of Natural History at Cassel, inviting the Academy to send a delegate to their semi-centennial jubilee; and from J. van Beneden, acknowledging his election as Foreign Honorary Member.

The President announced vacancies occasioned by the death of Mr. Henry P. Kidder, Treasurer, and the resignation of Mr. N. D. C. Hodges, Librarian. These vacancies were filled by the election of the following officers:—

AUGUSTUS LOWELL, *Treasurer*.

HENRY W. HAYNES, *Librarian*.

On the motion of Professor Cooke, it was

*Voted*, That the following proposed alteration of the statutes be referred to a committee: that the Librarian be *ex officio* a member of the Council.

The President appointed Messrs. Scudder, Gray, and Cooke members of this Committee.

Emil Heinrich Du Bois-Reymond, of Berlin, was elected a Foreign Honorary Member in Class II., Section 3, in place of the late Gabriel Gustav Valentin.

The following paper was presented:—

Equal Temperament and its Realization on Keyed Instruments. By Charles R. Cross.

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Seven hundred and ninety-first Meeting.

April 14, 1886. — MONTHLY MEETING.

The PRESIDENT in the chair.

Mr. Haynes was appointed Recording Secretary *pro tempore*.

Professor Safford presented a paper on Star-places observed at Williams College Observatory in 1884, with remarks on the present fundamental catalogues.

Mr. Edmands spoke of a device to do away with the collimator lens.

Mr. Sereno Watson presented the following papers:—

Preliminary Synopsis of North American Carices. By L. H. Bailey, Jr.

Contributions to American Botany:—1. Revision of the North American Ranunculi. 2. Sertum Chihuahuense, an account of collections of plants made in Chihuahua, by C. G. Pringle and Edward Palmer. 3. Miscellanea. By Asa Gray.

Contributions to American Botany:—1. A List of Plants from Southwestern Chihuahua, Mexico, collected by Dr. E. Palmer, 1885. 2. Descriptions of New Species of Plants, chiefly from the Pacific States and Chihuahua. 3. Notes upon some Polypetalæ and Palms of Eastern Guatemala. By Sereno Watson.

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Seven hundred and ninety-second Meeting.

May 12, 1886. — MONTHLY MEETING.

The PRESIDENT in the chair.

The Corresponding Secretary read a letter from Emil Du Bois-Reymond, acknowledging his election as Foreign Honorary Member.

The following papers were presented:—

A biographical notice of the late Edward Tuckerman. By Asa Gray.

The Crystalline Structure of Iron Meteorites. By Oliver W. Huntington. (By invitation.)

A Catalogue of Polar Stars for the Epoch 1875.0 resulting from all the available Observations made between 1860 and 1883, and reduced to the System of the Catalogue of Publication XIV. of the Astronomische Gesellschaft. By William A. Rogers and Anna Winlock.

Professor Gray presented the following paper by title:—

Notes on Arctic Algæ. By William G. Farlow.

Professor Cooke presented, by title, the following papers:—

On a Relation between the Formation of Anilides and the Constitution of Unsaturated Fatty Acids. By Arthur Michael.

Same title (second communication). By A. Michael and G. M. Palmer.

On the Action of Anilines on Brommaleic and Bromfumaric Acids. By A. Michael.

On Isomerism in the Cinnamic Acid Series. By A. Michael and G. M. Browne.

On Alloisomerism. By A. Michael.

Citraconic Acid as a Reagent for the Detection and Separation of Aromatic Amines. By A. Michael.

The Conversion of *α*-Bromocinnamic Ether into Benzoylacetic Ether. By A. Michael and G. M. Browne.

On the Action of Phosphorous Pentachloride on Organic Ethers. By A. Michael.

On the Action of Phosphorous Pentachloride on Phenoxyacids. By A. Michael.

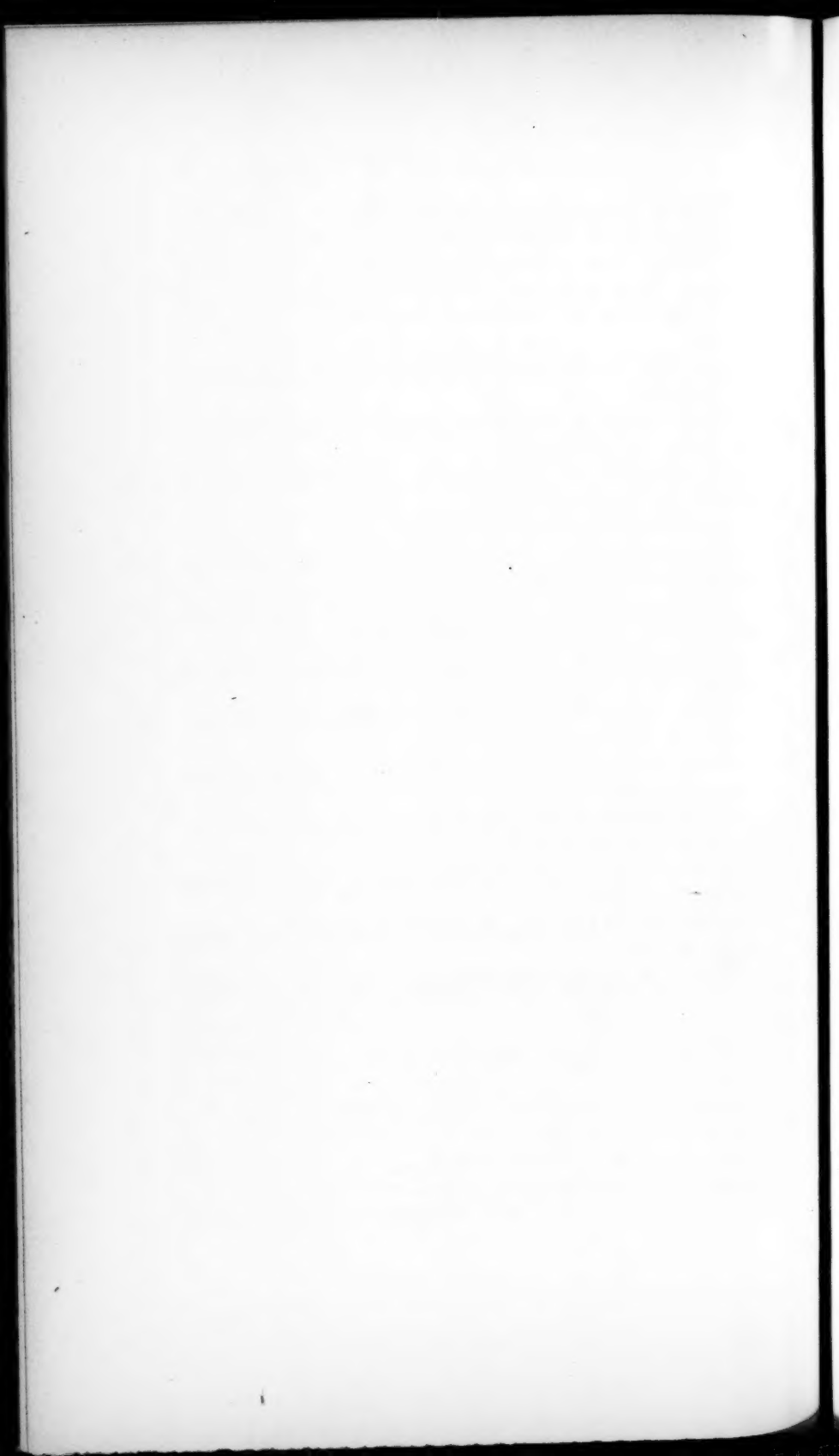
On the Action of Aldehydes on Phenols. By A. Michael and J. P. Ryder.

On the Action of Picrylchloride on Sodium Acetate. By A. Michael and J. P. Ryder.

On Mono- and Dipicrylhydroxylamine. By A. Michael and G. M. Browne.

A Method for preparing Bromderivatives of Fatty Acids. By A. Michael.

On the Ethylmethylenedisulphonate. By F. O. Kendall.



## REPORT OF THE COUNCIL.\*

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MAY 25, 1886.

During the last year the Academy has lost by death ten members;—viz. eight Resident Fellows: W. S. Clark, Charles E. Hamlin, Henry P. Kidder, Robert Treat Paine, H. H. Richardson, C. U. Shepard, John L. Sibley, and Edward Tuckerman; and two Foreign Honorary Members, Henri Milne Edwards and Leopold von Ranke.

### RESIDENT FELLOWS.

SAMUEL CABOT, M.D.

DR. CABOT was born in Boston on the 20th of September, 1815, and always resided in Boston or the neighboring town of Brookline. He was the second son of Mr. Samuel and Mrs. Eliza (Perkins) Cabot.

On his father's side, he belonged to a family distinguished in political and social life. His mother was a daughter of one of those noble merchants who have made a generous use of their great wealth, and are remembered in the gifts due to their generosity. The "Perkins Institute and Massachusetts School for the Blind," which owes its existence to the liberality of Thomas Handasyd Perkins, is the enduring monument of the maternal grandfather of Dr. Cabot.

The subject of this notice was fitted for college at the Boston Latin School, entered Harvard University at the age of seventeen, and was graduated in 1836. He was not distinguished as a scholar during his

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\* The decease of Richardson and Von Ranke has been too recent to admit of notices in this volume; but notices of Cabot, Dixwell, Hooper, and Von Siebold, omitted for the same reason last year, are now given.

college course. He was far from idle, but he chose his own kind of industry. Students were not allowed to keep fire-arms, but young Cabot would often visit Fresh Pond early in the morning and bring back a duck or two, showing that he knew how to use a gun effectively. His father called at Cambridge one day, and was told by his son's friend, Amos Lawrence, that such was his habit, and that if he called in the evening, when he would be welcome, he would probably find a duck roasting at the end of a string which he might notice hanging in front of the fireplace. His father then spoke of Sam's facility in stuffing birds, and as he went away he said, "Perhaps he will make a naturalist, or at least an ornithologist."

In 1839 he took his medical degree at Harvard, after which he went to Paris, where he remained two years, continuing his medical studies. The fondness for ornithology which he had shown in his college days lasted through all his subsequent life. In 1842 and 1843 he accompanied Mr. John Lloyd Stephens in his explorations in Yucatan, and worked up the ornithology of the expedition for Mr. Stephens's "Incidents of Travel" in that country.

Dr. Cabot settled in Boston as a practitioner in surgery and medicine, and took a high place in the profession. In the mean time he never forgot his favorite branch of science. He was appointed Cabinet-keeper of the Boston Natural History Society in 1839, and had especial charge of the collection of birds belonging to the Society from 1844 to 1854.

In 1853 he was appointed a surgeon of the Massachusetts General Hospital, in the place of the late Dr. John Collins Warren. "How faithfully he served," says Mr. Lawrence, "all who were associated with him, and all who came under his care, knew well. His kind heart sometimes made his duties arduous"; and Mr. Lawrence relates an instance in which his humanity and self-reliance were put to the severest test, and proved equal to it.

As a surgeon Dr. Cabot was highly esteemed for his skill and conscientious attention to his patients. He was one of the first, if not the very first, in this country to perform the subcutaneous operation for strabismus. Impulsive, excitable, self-reliant, full of generous impulses, not always remembering the *suaviter in modo* as well as the *fortiter in re*, he was one of those men whom every friend—and every enemy, if he had any—would always know where to find. Everywhere a sturdy champion of the right as he conceived it, his sympathies with the weak, the oppressed, the sick, the suffering, could always be counted upon; and his fiery indignation against the oppressor, against

all who were false to the claims of humanity, was always ready to declare itself with unmistakable energy. All these personal qualities showed themselves in his relations with his patients and his brother practitioners, and leave the impression of his virile and full-blooded nature deeply stamped upon their memory.

A practitioner at once skilful, humane, and widely known and trusted, is all his life long doing charitable work for his fellow-creatures. It is pre-eminently true of the benevolent surgeon, that his left hand never knows half that his right hand doeth. But private acts of mercy and kindness were not enough for the warmly benevolent nature of Dr. Cabot. As President of the Infant Asylum, and as physician to the Home for Destitute Children, which latter office he held for thirty years, he consecrated his professional skill to public uses. He took an active part, as a member of the Emigrant Aid Society, in the settlement of Kansas. This is not the place to tell the story of that eventful period; but if it were told, the energy and the sacrifices of Dr. Cabot would form a notable part of the record. Mr. Lawrence, who was his early friend and his collaborator in this as in other good works, says of him: "Dr. Cabot was a philanthropist in the best sense. He never wearied until the good object was accomplished, and he never sought to exalt himself at the expense of his associates. His humility was as conspicuous to his friends as his merit was to them and to all who acted with him."

With the exception of two visits made to the army during the war of the Rebellion, Dr. Cabot continued to practice medicine in Boston until the period of the illness which ended in his death on the 15th of April, 1885.

Dr. Cabot was elected a member of this Academy in Class II., Section 3, in the year 1844; he was also a member of the Massachusetts Medical Society. During his long connection with the Boston Society of Natural History, from the year 1830 to the year of his death, Dr. Cabot made many communications to the Society, the most important of which are enumerated in the following list.

*Proceedings.*

Vol. I. On *Meleagris ocellata*. On *Phasianus motmot*. On the Wild Turkey. On *Ortyx nigrogularis*. New Birds of Yucatan. On Palmated Horns in *Curvus Virginianus*. Senotes of Yucatan.

Vol. II. On *Pica melanoleuca*, Magpie. New Species of Humming-Bird. On the Anatomy of *Fuligula spectabilis*. On the European and American Widgeons. On *Tetrao cupido*. On *Pyrranga roseo-gularis*. On *Sterna cantiaica*. On *Troglodytes albinucha*.

Vol. III. On the American and European Oyster-Catcher. On *Ibis guarauna*.

Vol. IV. Notes on the Internal Anatomy of a Female Mina Bird (*Gracula religiosa*).

Vol. V. Wild Hybrid Duck propagated between the *Clangula Americana* and the *Mergus cucullatus*.

*Journal.*

Vol. II. Observations on the Plumage of the Red and Mottled Owls.

Vol. IV. Observations on the Characters and Habits of the Ocellated Turkey (*Meleagris ocellata*). Description and Habits of Birds of Yucatan.

Vol. V. Further Accounts of Birds of Yucatan. Description of *Pyrrangula roseo-gularis*. The Dodo a Rasorial and not a Rapacious Bird.

WILLIAM SMITH CLARK, M. A., PH. D., LL. D.

WILLIAM SMITH CLARK, M. A., Ph. D., LL. D., son of Dr. Ather-ton and Harriet (Smith) Clark, was born, July 31, 1826, at Ashfield, Mass., and received his early education there and at Williston Seminary, Easthampton. Graduating from Amherst College in 1848, he returned to Williston Seminary, where he taught the natural sciences from 1848 to 1850. He then went abroad, and for the next two years devoted himself to the study of chemistry and botany at Göttingen, Germany, receiving from that University the degree of Ph. D., in 1852.

On his return to this country, he was elected to the Chair of Chemistry, Botany, and Zoölogy in Amherst College, performing the duties of that position from 1852 to 1858, and of the Chair of Chemistry alone from 1858 to 1867, when he resigned to accept the Presidency of the Massachusetts Agricultural College. This, and the Professorship of Botany and Horticulture, he held from 1867 to 1879. He then became interested in the project of a "floating college," and being made President, bent all his energies, during the years 1879 and 1880, to developing this scheme of uniting scientific study with a trip round the world. It was abandoned, however, on the sudden death of its originator, Mr. Woodruff. He subsequently engaged in mining operations; and the last few years of his life were spent quietly at his home in Amherst, vainly battling with the disease which had already sapped the foundations of his life. He died at his home, on March 9, 1886, from an affection of the heart.

At the breaking out of the war, in 1861, he hastened from the lecture-room to offer his services in the field, and received a commission as Major in the 21st Massachusetts Volunteers, in August, 1861.

A born leader of men, he was quickly promoted to be Lieutenant-Colonel, February, 1862; Colonel, May, 1862; and was recommended by General Burnside "for a well-deserved promotion" as Brigadier-General, in September of the same year. He participated in the battles of Roanoke Island, Newbern, Camden, N. C., the second battle of Manassas, Chantilly, the Antietam, and Fredericksburg. It was at the battle of Chantilly that, losing his way and becoming separated from the regiment, accompanied by only a handful of men, he was surrounded by the rebels and ordered to surrender. Preferring to run every risk rather than encounter the horrors of Andersonville or Libby, a desperate effort was made to escape, but all were shot down except himself. Bullets whistled through his cap and clothing, but unhurt he reached the cover of the woods, and lay concealed within the enemy's lines for three days, suffering from hunger and exposure, until finally he reached the Union forces in safety, and was welcomed as one returned from the dead, for he had been reported among the fallen.

His was a busy life, spent in the service of others. Never for a moment did he shrink from the duties of the hour, or hesitate to assume the responsibilities laid upon him. He was a member at large of the Massachusetts State Board of Agriculture from 1859 to 1861, and member *ex officio* from 1876 to 1879; one of a commission of three appointed by Governor Andrew to consider the expediency of establishing a State Military Academy, in 1863; Presidential Elector and Secretary of the Electoral College in 1864; Representative to the legislature in 1864, 1865, and 1867; and trustee of several academic institutions. While still connected with the Massachusetts Agricultural College, he was invited by the Japanese government to establish and organize the Imperial College of Agriculture, at Sapporo, Japan, and during the two years (1876-77) of his residence there continued to preside over the interests of both colleges. The same success that attended his efforts at home followed him abroad, and he gathered about him a corps of enthusiastic teachers and students which has made the college a most important factor in the educational force of the country. With his trained eye and keen powers of observation, he was quick to perceive, amid the new Flora by which he was surrounded, those plants worthy of being introduced into this country; and among those he was instrumental in thus introducing may be mentioned the beautiful deciduous shade tree, the *Cercidophyllum Japonicum*, the vigorous and hardy *Actinidia arguta*, and the climbing *Schizophragma hydrangoides*. In addition to these, he sent home from Northern Japan a

large assortment of seeds of plants already known, but of special value to Massachusetts from the high latitude from which they were selected. Nothing escaped his scrutiny; and on the side of Mount Tieni, at an elevation of 3,200 feet, he discovered a new lichen, named by Professor Tuckerman, in his honor, the *Cetraria Clarkii*. The seeds of the umbrella pine, the *Cladopetis verticellata*, which previous to his visit it had been difficult to obtain on account of the veneration in which the tree was held by the natives, he procured in large quantities, sending a man far up into the mountains to fell a tree and gather the cones before they opened and scattered their seeds.

President Clark received the degree of LL. D. from Amherst College in 1874. He had been a Fellow of the American Academy of Arts and Sciences since 1868, was a member of the Massachusetts Horticultural and New England Agricultural Societies, honorary member of the Massachusetts Society for promoting Agriculture, and resident member of the New England Historic Genealogical Society. He was author of the following papers in Liebig's *Annalen*: "Ueber Chlormagnesium-Ammoniak," 1851; "Analyse des Steinmarks aus dem Sächsischen Topasfels," 1851; and "Analysen von Meteoreisen," 1852. He contributed the following articles to the Annual Reports of the Massachusetts State Board of Agriculture: "Report on Horses," 1859 and 1860; "Professional Education the Present Want of Agriculture"; "The Work and the Wants of the Agricultural College," 1868; "The Cultivation of Cereals," 1868; "Nature's Modes of distributing Plants," 1870; "The Relations of Botany to Agriculture," 1872; "The Circulation of Sap in Plants," 1873; "Observations on the Phenomena of Plant Life," 1874; and "Agriculture of Japan," 1878. He translated, for use in the Massachusetts Agricultural College, the Blow-pipe Manual of Professor Scheerer, 1869.

Following the investigations of Hales in the early part of the eighteenth century, he carried on a series of novel experiments, in 1873-74, relative to the circulation of sap in plants, and the expansive force exerted by the vegetable cell in its growth. The squash he had selected for observation, in its iron harness, lifting five thousand pounds before it ceased to grow, excited attention far and wide, and was visited by hundreds. But his best work was as an educator. The years spent as Professor in Amherst College and as President in the Massachusetts and Japanese Agricultural Colleges were not in vain. Bringing to the lecture-room that intense enthusiasm and personal magnetism so characteristic of the man, he quickly established a bond of sympathy between teacher and scholar that was never broken. He

infused his own buoyant nature into all with whom he was brought in contact, and reduced to a minimum the strained relations of pupil and instructor. The same brilliant qualities that attracted men in the outside world made themselves felt in his teaching. The dry details of science were enlivened by the light play of his fancy, and the charming method of his teaching seldom failed of arousing the dullest intellect. Frank, impetuous, and generous, he was welcomed everywhere; and none more sincerely mourn him than those who knew him best as teacher, soldier, and associate.

He was married, May 25, 1853, to Harrietta Keopuolani Richards, daughter of Rev. William Richards, of the Sandwich Islands, and adopted daughter of Samuel Williston of Easthampton.

#### GEORGE BASIL DIXWELL.

GEORGE BASIL DIXWELL was born in Boston on the 15th of December, 1814, being the third son of John Dixwell, M. D., H. C. 1796. He was fitted for college at the Boston Public Latin School, and passed the examination for admittance to Harvard in 1830. Although an excellent scholar and very promising in all departments of study, circumstances induced him to adopt a commercial career; and, after a thorough preliminary training in a counting-house, he accompanied his elder brother to India, and there began the life of a merchant, which he pursued with few intermissions for the remainder of his life, partly in Hindustan, but principally in China. His early education and his natural bias turned him to the acquisition of languages and to the study of mathematics. He became an expert in the Hindustani, and used it in his commercial intercourse with the natives of India. Afterwards, while in China for about fifteen years, he studied the Mandarin dialect, and became an accomplished speaker and writer of that language.

He was for several years the Russian Consul-General at Hong Kong, and he was also for some time the head of the municipal government at Shanghai.

He had a strong bias toward scientific investigation, and cultivated the mathematics and physics, and later in life paid much attention to dialectics.

On his final return to America in 1873, he entered on a course of investigation and experiment in regard to the use of superheated steam, with results which were hailed by some scientists as of very great value in view of practical improvement in the use of the steam-

engine and the great economy of fuel. These results were published.\* Latterly, however, with American versatility, he turned his attention almost exclusively to the subject of political economy. Approaching the subject from the practical side, with a life's experience in the processes of commerce, and with a reach of mind gained by a world-wide survey of the affairs of all nations, and with a masterly comprehension of the works of the other economists, he deliberately and dispassionately, but steadfastly, adopted the views of the protectionists. He wrote much on that side of this important question of American policy, and favored all means of defending our interests against the aggressions of British manufacturers. His articles and pamphlets were distributed gratuitously by him to all public libraries and colleges in the Union, and to many private persons who were interested in the subject therein discussed.

His style is vigorous, logical, and terse; and he wrote with firm conviction, generous impulses, and with views, as he thought, far-reaching for the welfare of his country.

He died in Boston, of pneumonia, on the 10th of April, 1885, after an illness of a few days, at the age of seventy years and four months.

#### CHARLES EDWARD HAMLIN.

CHARLES EDWARD HAMLIN, who was for more than twelve years connected with the Museum of Comparative Zoölogy, Harvard University, died at his home in Cambridge, January 3, 1886, after an illness of between two and three months, ending in acute pneumonia complicated with other disease. He was in the sixty-first year of his age, having been born in Augusta, Maine, February 4, 1825. Graduated from Waterville College, now Colby University, in 1847, he was during the next six years successively a teacher in schools of high grade at Brandon, Vermont, Bath, Maine, and Suffield, Connecticut. He was then appointed Professor of Chemistry and Natural History at Waterville, and for twenty years remained at this post an ardent and successful teacher of these subjects, often, however, assisting in

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\* A Paper on Cylindrical Condensation, Steam Jackets, Compound Engines, and Superheated Steam, by George Basil Dixwell. Read before the Society of Arts at the Massachusetts Institute of Technology, Boston, April 29 and May 13, 1875. Printed at Boston, 1875.

Report of Engineers of the U. S. Navy upon Experiments with Saturated and Superheated Steam made at the Massachusetts Institute of Technology, March, 1877. Printed at Boston, 1877.

other departments as occasion required. For a long period he kept the obituary record of the Alumni Association of his college, and continued to the end one of the most esteemed and beloved friends and counsellors of the institution.

So faithful was the young Professor to his work, and so earnest to maintain the standard of his knowledge at the level of the most recent advances in the branches which he taught, that, for several years after his appointment at Waterville, he spent his winter vacations in practical scientific study at the laboratories of Harvard University, — first in the Chemical Department under Professor Cooke, and afterwards in the Department of Zoölogy under Professor Agassiz. He thus acquired such a love for scientific investigation that, in 1873, he removed to Cambridge, accepting an appointment as Assistant in Conchology and Palæontology in the Museum of Comparative Zoölogy. During one or two of the earlier years in his new home he gave instruction in geography and geology; but he soon relinquished teaching, and was occupied solely with his work in the Museum, the traditions of whose founder were congenial to his spirit. An invitation in recent years to resume his old position at Waterville, as well as a similar overture from Brown University, was declined; but he constantly attended the "Commencements" of his college, where he was always received with a hearty welcome. In 1873 he was honored with the degree of LL. D. from the University at Lewisburg, Pennsylvania, and in 1880 he was appointed one of the Trustees of the larger institution, now called Colby University, into which his well-beloved college had grown.

Professor Hamlin was an enthusiastic explorer of his own State, and was especially familiar with Mount Katahdin, which he often visited, and of which he made a model to illustrate his long and delightful studies of that mountainous region. Some years before his death he enjoyed the pleasure and advantages of a journey in Europe, and he greatly improved the opportunity for his own cultivation, as well as for the benefit of the department of the Museum which he had in charge. Professor Hamlin was a student rather than a writer; but he published several occasional papers, among which may be mentioned, "Observations during Visits to Mount Katahdin, Maine"; "A Report of an Examination of Syrian Fossils" (a collection sent to the Museum by the Rev. Selah Merrill, D. D., while U. S. Consul at Jerusalem); and, lastly, "The Attitude of the Christian Teacher in Respect to Science" (an address read before an educational convention of his own denomination at Worcester, Mass., in 1871).

Our associate's excessive modesty and shrinking from publicity led to a retired life, and comparatively few enjoyed the profit and charm of his familiar acquaintance. These, however, could testify to the breadth and catholicity of his tastes and sympathies, which were not less marked than his ardor and capability in his own special labors. If natural science was his vocation, ancient and modern literature and antiquarian research were his avocations; nor with all the simplicity of his life was he a stranger to the luxury of charity. In short, it was the happy instinct of this amiable and modest man to conform his life to Wordsworth's ideal for the student of science, — that he should also be enriched and gladdened by converse with poets, sages, and men of letters. He was a consistent and devout Christian, greatly beloved and respected in the Baptist Church, to which he was devotedly attached.

#### ROBERT WILLIAM HOOPER.

ROBERT WILLIAM HOOPER, son of John and Eunice (Hooper) Hooper, was born in Marblehead, Mass., October 25, 1810. He was graduated at Harvard College in the year 1830, and in 1833 went to Europe, where he studied medicine. After pursuing his studies in Paris and elsewhere, and after travelling over a large part of Europe, he returned to America in 1835, took his degree of M. D. from Harvard College in 1836, and began the practice of his profession in Boston. He married, September 25, 1837, Ellen, eldest daughter of William Sturgis, merchant of Boston, and Elizabeth Marston (Watson) Davis, his wife. Three children, all of whom survived their parents, were born of this marriage. Mrs. Hooper died on November 3, 1848.

For nearly fifty years after beginning the practice of his profession, Dr. Hooper lived in Boston, devoting himself to his family and friends and to the public institutions with which he was connected. His private practice was never large, but his sphere of usefulness was not confined to his profession. He was one of the surgeons of the Massachusetts Charitable Eye and Ear Infirmary, and its records show that he had "for more than a generation been connected with its development and watched over its interests." For thirty years he was one of the trustees of the Boston Athenæum, and his associates have said that "he has worked himself, he has interested others and made them work, and he has done more than any one else to build up the library, increase its value, and extend its usefulness." For twenty-seven years

he gave much of his time to the care of the State Hospital for the Insane at Worcester, of which he was a trustee. Though his professional income was small, and his services were for the most part gratuitous, he enjoyed by inheritance, and increased by prudent management, a property sufficient, and in his later years more than sufficient, for his always moderate wants. His religious feelings, rarely expressed except in his personal character and conduct, were strong and constant.

He died, after a short illness, at the house of his son-in-law, Professor Gurney, at Cambridge, on April 13, 1885.

#### HENRY PURKITT KIDDER.

HENRY PURKITT KIDDER, lately the Treasurer of the American Academy, was born in Boston on the 18th of January, 1823. His father was Thomas Kidder, of that city. His mother, Clarissa Purkitt Kidder, was the daughter of Henry Purkitt, one of the Boston mechanics who were united in the Tea Party of December 16, 1773. He afterwards served in Pulaski's cavalry corps. His grandson was proud to inherit his name.

Henry Purkitt Kidder was one of several children. He passed through the lower schools, and, not many years after the establishment of the English High School, then kept in Pinckney Street, Boston, in a house built for it, he went through the full course of that school. He was first under the charge of Solomon Pearson Miles, and afterwards of Thomas Sherwin. To these gentlemen, and to George Barrell Emerson, their predecessor, all members of this Academy, was given, to a large degree, the formation of the system which has since prevailed in New England, in what in Europe has been called "Secondary Instruction,"—the system of those high schools which do not attempt training in the classics. From the first, the English High School, under the lead given by these masters, has taken a high standard, and its method and discipline have been widely copied.

Mr. Kidder always looked back with pleasure upon the years which he spent there. In after life he gave to the school association, in memory of his school life, the group of statuary which now stands in the broad entrance hall of the schoolhouse. He brought from the school a quick ability in the mathematics, a taste for general literature, which he cultivated to the end of his life, a tolerable working knowledge of the French language, and the rudiments of the training for mercantile business which gave to him afterwards a happy and successful life.

He is remembered with pleasure by his school companions as a kindly, good-natured boy, willing to play, but as willing to study, conscientious and unselfish. But I doubt if any of them then knew or guessed that he had the qualities which would make him a leader among his fellow citizens before he died.

When he left school, he sought and obtained at once a boy's place in the auctioneer's firm of Coolidge and Haskell. Boys trained in the English High School were then, and always have been, favorites among Boston merchants, and this young fellow made good the reputation which his comrades had won. From the service of this firm he passed to that of the Boston and Worcester Railroad, in which he was a freight clerk until he was twenty-one years of age.

He had always wished to see the Western country, as does every young man of spirit in America, and had perhaps dreamed of establishing himself there. So soon, therefore, as he was free to choose his own life and career, he went to New Orleans, where he had a sister married, and from New Orleans went up the Mississippi River to Cincinnati, not travelling rapidly, but inquiring from place to place whether there were any need of him. If need there were, it did not show itself, and he was fond of saying in after life that the best lesson he ever learned, or the best perhaps but one, was that which he taught himself, or which a kind Providence taught him, when in Cincinnati he found he had expended all his money but a quarter of a dollar, and was, to appearance, no nearer finding his life-work than when he began his adventure. The truth was, that a certain instinctive purity of life made him dislike, with a certain shudder, the low or rough companions whom he was thrown with in the adventures of a young steamboat traveller in "prospecting," and the precise training for accurate business which led in fact to the career which he followed in after life was not exactly the discipline which would help him best in the rough give-and-take of life in new communities. However this may be, he came home to Boston, as soon as his friends sent him money for that purpose, wiser than he had started, and poorer, and wholly indisposed from that time to seek his home in other communities.

It was not long before he engaged himself as a junior clerk in the banking house of the late Ebenezer Francis, — the same house which was afterwards known as John E. Thayer & Co., and later yet, under Mr. Kidder's lead, took the name it still bears, of Kidder, Peabody, & Co. Mr. Francis had been the treasurer of Harvard College; he was also the treasurer of the Academy for many years, as was his

son-in-law Mr. Thayer after him, whom Mr. Kidder in his turn succeeded in the watchful care of our modest funds. It may be said, in passing, that the life of Ebenezer Francis would be a curious and might be an interesting addition to the history of the growth of the town of Boston, and would mark the steps by which the little town opened its communications with the West, and made the sudden growth in population and wealth which followed fast on the incorporation of the city. Mr. Francis was the son of the Colonel Francis who was killed at the head of his regiment when charging the English for the third time, as he covered St. Clair's retreat before Burgoyne. Burgoyne's despatches speak of Francis as "one of their best and bravest officers."

The private bank of Ebenezer Francis was small in comparison with the banking institutions of to-day. When Mr. Kidder entered it, it was largely directed by the brothers Thayer, one of whom had married Mr. Francis's daughter. The great railway enterprises of the country were beginning, and, after the natural timidity of capitalists had been conquered by the courage and success of adventurers, the brothers Thayer had joined wisely in their promotion. Mr. Kidder, entering as a beginner, stated at once to his young friends the rule in life which he afterward often urged on another generation. The success of the firm, he said, was his success, and it was his place to see it succeed. Very early in his connection with the house he was able, in his subordinate place, to discern methods of enlarging its work which instantly approved themselves to the sagacity of the brothers Thayer. They saw, and were glad to see, what manner of man they had in their employ, and advanced him rapidly in confidential positions.

From early life he was ready, was determined indeed, to do his part, whatever it might prove to be, for the community in which he lived. But he was modest and would never push himself as an applicant for any public trust, and it happened—not unnaturally perhaps—that the first public function he was ever asked to assume was that of teacher in the Sunday school, if indeed that can be called a public function. But the duty should be spoken of here, because, in the crowd of public trusts afterward imposed upon him, he had to say that the first time any one asked him to "be" anything was when he was asked to be a teacher in a Sunday school, and the second was when he was asked to serve as the youngest member of the church standing committee. To each trust he would carry a sensitive, perhaps a proud conception, of what it is to be asked by other men to fulfil a duty for the general good; and, as his life went forward, his readi-

ness to be of use, and his distinct recognition of the truth that he was in the world to be of use, and for nothing else, made him accept even the most difficult commissions, so he were only sure that the business in hand was something in his line, something which filled a public necessity, and something which he would do well.

He was thirty-eight years old when the war struck the country, and tested every man and woman in active life. Many of Mr. Kidder's immediate associates went to the field. His brother was killed, at the head of his company, in the battle of the Wilderness. In the thousand home duties, hardly less exciting, and certainly when wrought out by such men not less useful to the country, he was of service everywhere. His counsel was sought and given, his executive powers were freely devoted to every effort for the strengthening of the country, and wherever a strong man of affairs could serve, in that place he might be found.

He was for some years a junior partner of the firm of John E. Thayer & Co., and when Mr. Nathaniel Thayer retired from active business, in 1865, Mr. Kidder, Mr. Frank Peabody, and Mr. Oliver Peabody formed the new firm of Kidder, Peabody, & Co., which exists at this time. Just before Mr. Kidder's death, the firm was connected with the firm of Baring Brothers, which in the history of finance and of politics has for nearly a century been an important link in the union of the United States and Great Britain.

A man who had so much to do with the development of the physical resources of the country may fairly be said to be connected in the closest way with its practical science. But it is rather as an enthusiastic patron of the fine arts that Mr. Kidder deserves his place as a prominent member of the Academy of Arts and Sciences. In early life he began the collection of prints, which he afterwards enlarged by the purchase of choice examples. In such matters he was — what he would never have called himself — a connoisseur. But afterwards, as he was able to indulge his very admirable taste, he preferred to buy pictures generally of the artists of our own time, such as should give pleasure to himself and to his friends in his beautiful homes. No man was less apt to be led by a dealer than he. He would buy what he liked, and what he did not like he would not buy. He knew what he liked, and knew it with a very definite certainty.

This interest or passion is not to be spoken of without reference to his enthusiastic love for nature, his passion for flowers, and the pleasure which all fine scenery gave him. Some one asked him once what was his favorite summer amusement, and he replied, "Sitting on a

fence to see the grass grow." This was a simple and accurate enough statement of the pleasure which he took in gardens and gardening, in travelling in picturesque countries, and of the solid satisfaction which he took in natural beauty, whether simple or grand. Without the slightest facility of hand beyond the ability to make a neat geometrical drawing, he had much of the make-up of an artist, which showed itself both in his choice of pictures for his home and in the large amount of time and life which he really consecrated in the open air.

He was chosen into the American Academy on June 9, 1880; treasurer, on May 29, 1883. The surviving members will remember with interest the impressive exercises at his house on the evening when Mr. Corliss received the Rumford Medal, as well as other occasions when the Academy has enjoyed his hospitable welcome.

Mr. Kidder was a member of the government of the Massachusetts General Hospital, and of the Board of Overseers of Harvard College; he was President of the Unitarian Association, of the Children's Mission, and of many other charitable societies. It is interesting to say of a man so largely engaged in the public service, that he was superintendent of the Sunday school of the South Congregational Church for more than twenty years. His life, indeed, was freely given to the service of his fellow men.

When one has said this, he has said the most remarkable thing about his life, and has named the most remarkable feature in his character. He would himself have said that such success as had come to him in life was due to his determination to use life for the common service. But it must be added, that this firm moral purpose had so moulded his habits of daily work as to give him a power of command or leadership which does not fall to common men. While the city of Chicago was yet burning, a town meeting of the people of Boston was held to take measures for their relief. The Mayor presided, and read a list of officers whose names were suggested as a commission to collect and forward the contributions of Boston. Almost of course, Mr. Kidder was proposed as treasurer. A little after, he left the platform and went back to his bank. Within a few minutes came down from him this message to the Mayor: "I have bidden them draw on me at sight for \$100,000." The other speaking was interrupted, that this best speech of all might be repeated; and Faneuil Hall was never so enthusiastic as when it thus learned to what standard of liberality he had pledged them. In point of fact, the subscriptions of Boston amounted to more than half a million. It was that despatch of his which struck the key-

note for the liberality of the world. How it was received in Chicago you know. With us, the speaking went on from the platform ; and at the end of the morning we elected the list of officers who had been nominated two or three hours before. With his usual promptness, he had taken the whole responsibility before he was so much as chosen to the position in which he was formally acting.

Such promptness as this — his constant readiness to do a large thing rather than a small one — might, in a man of less balance or force, have become rashness. But of him it may certainly be said, that he acquired fortune without any apparent effort to acquire fortune ; he managed a host of trusts without any appearance of worry or anxiety ; he was always at ease and ready for companionship, — for literary, or musical, or other artistic gratification. In the midst of cares, he was never oppressed by them ; and while the least indolent of men, he never appeared exhausted. Such success reveals a well-disciplined mind of extraordinary power, and a soul master of that mind and of the body which served it, loyal to his God, willing to share in his work, and to seek his help to-day.

Mr. Kidder was twice married : first, to Caroline W. Archbald, in December, 1847. Mrs. Kidder died on the 31st of March, 1881, leaving him three sons, Henry Thomas Kidder, Charles Archbald Kidder, and Nathaniel Thayer Kidder.

He married a second time in June, 1883, Elizabeth Huidekoper, of Meadville, Penn., who survives him.

#### ROBERT TREAT PAINE.

ROBERT TREAT PAINE was born in Boston, October 12, 1803, and died in Brookline, June 3, 1885. He was the grandson of Robert Treat Paine, one of the signers of the Declaration of Independence, and afterwards Attorney-General and Justice of the Supreme Court of Massachusetts, and still better known as the eminent jurist who conducted the prosecution of Captain Preston and his men at their trial for committing the "Boston Massacre." The grandfather was a staunch Federalist, as was also the father, who bore the same name, and was esteemed in his day as a writer and poet. Mr. Paine, our associate, early displayed an interest in astronomy, and distinctly recollected being shown the comet of 1811. He never would admit that any later comet would compare with this, especially as regards the length of its tail, which extended from one side of the heavens to the other. This, like other astronomical objects, had in his mind a vivid

personality, to which he often referred in his conversation and letters. After graduating at Harvard College in 1822, Mr. Paine studied law, was admitted to the bar, and attained some prominence as a lawyer. He showed no desire for political office, although actively interested in politics and current affairs. He was a member of the Boston Common Council in 1828, 1833, and 1834.

While adopting the law as a profession, the great interest of his life was in the direction of astronomy and meteorology. Until his death this was his absorbing study, pursued with the greatest enthusiasm and occupying a large part of his thoughts and conversation. Without under-estimating the value of theoretical astronomy, Mr. Paine's special interest was in the practical side of this science. Soon after graduating at Cambridge he began a meteorological record, which he maintained with great regularity during the remainder of his life. The results for many years were communicated to the public through the columns of the *Boston Daily Traveller*. This record was maintained continuously for fifty years at one station, his house in Boston.

In 1875 Mr. Paine moved to Brookline, where he continued his observations until his death. The total record of nearly sixty years has rarely been equalled by a meteorological observer. Unfortunately, these valuable papers have all disappeared since his death. Mr. Paine's astronomical observations were made with portable instruments. With the sextant he attained extraordinary skill. When a survey of the State of Massachusetts was undertaken, in 1840, Mr. Paine was appointed chief engineer. He soon resigned the position, however, which was afterwards filled by Mr. Borden. All the astronomical work of the survey was done by Mr. Paine. He determined the latitude and longitude of twenty-seven places in the State with his sextant, and the results when compared with the triangulation of Mr. Borden showed a close agreement. The best evidence of the excellence of this work is, that it is still the most accurate determination of a large part of these stations. It is in fact employed as the basis of the new map of the State now being constructed by the United States Geological Survey.

Mr. Paine was associated with Jared Sparks and Joseph E. Worcester in the establishment of the *American Almanac*. He furnished the astronomical portion of this work from 1830 to 1842. Mr. Paine's greatest interest was in the motion of the moon, as determined by occultations and eclipses. During his life he computed over two thousand occultations. The first of these was the occultation of Uranus for Cambridge, September 2, 1824. Besides observing as many

of these occultations as he could, he observed three transits of Mercury and one of Venus. When a boy of nineteen, he computed the elements of all the eclipses of the sun visible in the city of Boston between the years 1822 and 1900. Mr. Paine spared no efforts to observe as many total and annular eclipses of the sun as possible. He succeeded in observing no less than nine, a record that has probably never been equalled by any other observer. Some of these observations involved great personal discomfort, or even danger; but no ordinary difficulties could daunt him when an eclipse was to be observed. Only a few months before his death he planned travelling alone to Montana to observe the eclipse of March 16, 1885.

The dates of the five annular and four total eclipses observed by Mr. Paine are as follows:—

1. Annular. Feb. 12, 1831. Lighthouse at Chatham, Conn. In order to reach this point Mr. Paine was obliged to make an inclement passage by sea of seven miles in an open rowboat.
2. Total. Nov. 30, 1834. Beaufort Arsenal, S. C.
3. Annular. Sept. 18, 1838. Capitol at Washington, D. C.
4. Annular. May 26, 1854. Middlebury, Conn.
5. Annular. Oct. 18, 1865. St. Michael's Church, Charleston, S. C.
6. Total. Aug. 7, 1869. Booneborough, Iowa.
7. Annular. Sept. 28, 1875. Brookline, Mass.
8. Total. July 29, 1878. Denver, Col. Mr. Paine describes his condition at this time as "sick and nearly blind."
9. Total. Feb. 15, 1880. Sycamore, Cal. Mr. Paine's indomitable energy is in no way better shown than by his observation of this eclipse. Although seventy-six years of age and comparatively infirm, he crossed the continent alone. On reaching his destination, he was left by the train on a treeless prairie, with no human being in sight or within many miles. The duration of totality was only thirty-seven seconds, and his main object was to determine this with certainty. He did not dare to devote any of this short interval to the examination of the grand physical phenomena visible only during a total eclipse, and therefore gave his attention exclusively to retaining the correct count of seconds by the chronometer. He returned, after his journey of six thousand miles, entirely satisfied, since he had secured his observations, although he can scarcely be said to have seen the eclipse.

Besides these central eclipses, Mr. Paine observed no less than fifteen partial eclipses of the sun from Boston and its vicinity. During sixty years no solar eclipse occurred in Boston which was not looked for by him, and observed, unless he was prevented by the weather.

Mr. Paine was a man of strong opinions, which he did not hesitate to express with the greatest freedom. He was constant to his friends, and never left an unjust criticism unanswered. He bitterly opposed any action in religion, science, or politics which he believed to be dishonest. He retained his strong will and excellent memory unimpaired to the last. His interest in his favorite science never failed him, and he showed his wish permanently to aid it by bequeathing his entire fortune to the Observatory of Harvard College.

## CHARLES UPHAM SHEPARD.\*

PROFESSOR SHEPARD died, after a short illness, on the 1st of May last, at Charleston, S. C., where for many years he had spent his winters. He was born in Little Compton, R. I., in the summer of 1804, and hence had nearly completed his eighty-second year. But until his last illness he was still young in his ardent devotion to his favorite science, his delight over the rare and beautiful among minerals, whether in his own cabinet or that of another, and his zeal for collecting and discovering new facts and new species; and not less young in his cheerful and kindly nature.

After graduating at Amherst College, in 1824, he became a student of Professor Nuttall's at Cambridge in botany and mineralogy, and soon after engaged at Boston in instruction in these branches. At the same time he commenced his publications on mineral localities and their minerals, in the *American Journal of Science*.

In 1827, Mr. Shepard accepted the position of assistant to Professor Silliman in chemistry, mineralogy, and geology, which he retained, to the great satisfaction of the Professor, for four years. While thus engaged he also continued, during leisure weeks, his field and laboratory work in mineralogy. "A Mineralogical Journey in Northern New England," including a study of the remarkable localities of Acworth, N. H., and Paris, Me., and "The Mineralogy and Geology of Orange County, N. Y., and Sussex County, N. J.," illustrated by a detailed map of the various mineral localities, are the titles of two of the many papers published by him at that time; and they indicate his desire to give others a knowledge of localities, as well as to make known the results of his investigations.

In 1832, Professor Shepard published the first part of a "Treatise on Mineralogy," in which the system of the eminent Austrian miner-

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\* From the *American Journal of Science*, June, 1886.

alogist, Mohs, was adopted as to nomenclature and as to the natural history idea of mineral species. The second or descriptive part of the work, containing the descriptions of the species arranged in alphabetical order, appeared in 1835. This delay in its publication was partly owing to Professor Shepard's acceptance from the general government, for the winter of 1832-33, of an appointment as an associate with Professor Silliman, for the investigation of the methods of sugar culture and manufacture in the Southern States, and to the preparation of his report on the subject, which was incorporated with that of Professor Silliman, made in 1833 to the Secretary of the Treasury. In the same year, 1835, he joined Dr. Percival, by appointment from the State legislature, in the Geological Survey of Connecticut; and two years later, in 1837, appeared his excellent report on the mineralogy and mineral products of the State.

His professorial work after 1832 was divided between New Haven, Conn., Amherst, Mass., and Charleston, S. C. To his duties at Yale, under Professor Silliman, were added those of Lecturer in Natural History, which position he held for fifteen years. From 1845 to 1852, and from 1861 to 1877, he occupied the chair of Chemistry and Natural History in Amherst College. In 1854, he was called to the Professorship of Chemistry in the South Carolina Medical College at Charleston; he continued there until 1861, and again resumed the duties of the chair in 1865, after the civil war, resigning them finally in 1869, when his son, Charles U. Shepard, Jr., was appointed his successor.

These university engagements interrupted but little his mineralogical work. His first new species, Microlite, was announced in 1835, Warwickite in 1838, and Danburite in 1839. Other discoveries followed these, occasionally of new species, often of kinds not before identified on the continent.

Professor Shepard's private collection of minerals, under so great personal activity, became large and choice, surpassing all others on the continent. On retiring from his professorship at Amherst the whole was purchased by Amherst College. Unfortunately, it passed from under his care to a building that was not fire-proof, and one night in 1880 it was nearly all destroyed. Professor Shepard did not cease collecting when he and his cabinet parted; but with his old zeal redoubled by the sight of empty shelves and drawers, he soon had again a large collection; and it continued to increase and to grow in interest with him to the close of his life.

Professor Shepard early commenced also the collection and study of meteorites, and through his life these shared with minerals in his affec-

tions and his labors. In 1829, nearly sixty years since, his first paper on the subject was published; and others followed, until the number reached nearly forty, the series closing with one in the last volume (September, 1885) of the *American Journal of Science*, to which he was thus a constant contributor during a period of over half a century. His collection grew, each paper being usually based on one or more acquisitions; and it was long the largest in the country. It became, like the minerals, and with them, the property of Amherst College.

Dr. Shepard's zeal to the end knew no flagging, and he had the satisfaction of seeing great progress in his two departments, that of meteorites and that of minerals, through his labors. His knowledge of mineral species was unsurpassed in the land; and he was hence ready with quick judgments as to new and old, — sometimes too quick, but in any case imparting progress to American mineralogy.

Dr. Shepard was several times in Europe, and had the personal acquaintance of many European mineralogists. He was a member of various American and foreign societies; among them, the Imperial Society of Naturalists of St. Petersburg, and the Royal Society of Göttingen. He was a man of refinement and great courtesy, and was held in very high esteem in Charleston, S. C., as well as at his Northern homes. His place of residence after leaving Amherst, and for much of his life before, was New Haven. He leaves two children, a son and a daughter.

#### JOHN LANGDON SIBLEY.

JOHN LANGDON SIBLEY, the eldest son of Dr. Jonathan and Persis (Morse) Sibley, was born in Union, Maine, December 29, 1804. He was fitted for Harvard College at Exeter, under the tuition of Dr. Abbot, and entered college in 1821. He held a good rank in his class, was rigidly faithful in all college duties, and at the same time commenced his life-work in the Library, then occupying the two rooms in the second story of Harvard Hall, and a little more than filling one of them. On graduating, in 1825, he received an appointment as Assistant Librarian; but at the end of one year the office was abolished, on the appointment of a Librarian who was expected to devote his whole time to his official duties. Mr. Sibley also entered the Divinity School in 1825, began to preach in 1828, became a pastor in Stow, Mass., in the following year, and resigned his pastorate in 1834. He then took up his residence in Cambridge, and engaged in several editorial and publishing enterprises, the chief of which was "The Amer-

ican Magazine of Useful and Entertaining Knowledge," patterned from the then very popular London Penny Magazine.

In 1841, on the removal of the College Library to Gore Hall, the office of Assistant Librarian was revived, and Mr. Sibley was appointed to fill it. In 1856, he succeeded Dr. Harris as Librarian in chief, and continued to discharge the duties of that office till 1877, when he retired from active service, on account of age and infirmity, retaining for the remainder of his life his official title with the prefix of *Emeritus*. During his administration, and in great part through his efforts and influence, the titles in the Catalogue of the Library, and the funds available for the purchase of books, were fully quadrupled.

Mr. Sibley edited ten successive Triennial Catalogues of the College, commencing with 1842, and a comparison of the Catalogue of 1839 with that of 1881 will show what a vast amount of fruitful labor was expended equally in improved method and in accuracy and fullness of detail. From 1850 to 1870 he edited the Annual Catalogue, and from 1870 to 1885 he prepared the annual Harvard Necrology, in these services manifesting the thoroughness and minute fidelity which with him were a matter of conscience fully as much as of habit.

Mr. Sibley was remarkable equally for his rigid simplicity and close economy in his own personal habits and expenses, and for the readiness and breadth of his charity. He had given more than thirteen thousand dollars to Phillips Exeter Academy, when the amount of these gifts considerably exceeded his remaining property. He was a benefactor, to a considerable amount, of Bowdoin College, of the Society for Preventing Cruelty to Animals, and of the Cambridge Hospital. At the same time, his private charities were not few or small, yet would undoubtedly have been larger, had he been aware of the extent to which for the last twenty years of his life his property had increased by the provident care and skilful investments of a friend, into whose hands he put what remained to him after his last Exeter benefaction. His was the singular case of a man who supposed himself possessed of less than half of the property which was actually his.

Mr. Sibley's working power, though impaired by illness and by partial loss of eyesight, continued until a few months before his death, which occurred on the 9th of December, 1885.

Besides articles in periodicals and contributions to the Proceedings of the Massachusetts Historical Society, Mr. Sibley's publications were, —

1. A History of the Town of Union, 12mo, 1851, pp. xii, 540.
2. Notices of the Triennial and Annual Catalogues of Harvard

University, with a Reprint of the Catalogues of 1674, 1682, and 1700, 8vo, 1865, pp. 67. This little book is full of materials interesting to antiquaries and to graduates of the College.

3. Biographical Sketches of Graduates of Harvard College, 8vo, Vol. I., 1873, pp. 618; Vol. II., 1881, pp. 557; Vol. III., 1885, pp. 457. These volumes contain the life-records of the graduates from the first Commencement to that of 1689 (inclusive). They represent an amount of patient industry and successful research almost unequalled. They contain all that could, or ever can, be learned of such of the graduates as were obscure or sublimous, while they give succinct and complete biographies of such of the list as were eminent in their time, few of whom have elsewhere Lives that are easily accessible or readable. The work done in these volumes could not have been better done, nor at a much later period could it have been done at all, so rapidly are records and traditions of earlier generations passing out of sight and fading from memory in our fast age. Mr. Sibley has left valuable materials for the continuation of his work, for which he has provided in the testamentary disposition by which his property will ultimately come into the possession of the Massachusetts Historical Society.

#### EDWARD TUCKERMAN.

On the 15th of March last, the Academy lost one of the older and more distinguished members of the botanical section, the Lichenologist, EDWARD TUCKERMAN.

He was born in Boston, December 7, 1817, was the eldest son of a Boston merchant of the same name and of Sophia (May) Tuckerman. He was prepared for college at the Boston Latin School, whence, in obedience to his father's choice rather than his own, he went to Union College at Schenectady. Entering as a Sophomore, he took his B. A. degree in 1837. He then entered the Harvard Law School, took his degree in 1839, and remained in residence in Cambridge for a year or two longer. In the year 1841 he went to Germany and Scandinavia, going as far north as Upsala, devoting himself, as in a subsequent visit, to philosophical, historical, and botanical studies. On his return, in September, 1842, he made, with the writer of this notice, a botanical excursion to the White Mountains of New Hampshire, with which he was already familiar. At the close of that or early in the following year he took up his residence at Union College, proceeded to the M. A. degree, and there prepared and privately published one of the smaller, but more noteworthy, of his botanical papers.

In the year 1844 or 1845 he returned to Cambridge, and in the autumn of 1846, in his twenty-ninth year, he became again an undergraduate. Applying for admission to the incoming Senior Class, he remarked to President Quincy that his father had broken the family tradition by sending him to another college, and that he proposed to correct the mistake. To the suggestion, that, being already an alumnus of the Law School as well as of Union, the University would willingly concede to him the earlier degrees he sought, he replied that he proposed to receive them in the ordinary way. He accordingly passed the regular examinations, took the whole routine of the studies of his class, and so was graduated with distinction in the class of 1847, — a unique but characteristic illustration of a loyal spirit, becoming "Small by degrees and beautifully less."

His passion for university study was not yet quite satiated. For, two or three years later, he entered the Harvard Divinity School, passed through its course of study and of prescribed exercises, — among them the delivery of a sermon in one of the Cambridge churches, — and so, in the year 1852, he became for the third time an alumnus of Harvard.

In May, 1854, he married in Boston Sarah Eliza Sigourney Cushing, who survives him, without offspring. Removing that year to Amherst, he built, with excellent taste, upon a beautiful site, the house which has ever since been their abode. Although mainly devoted to botanical investigations, his first official connection with Amherst College was that of Lecturer in History, then that of Professor of Oriental History, down to the year 1858, when he was collated to the chair of Botany, which he held to the end of his life, although of late years relieved from the duty of class instruction. The College did itself the honor to confer upon its Professor the degree of LL. D.

We cannot say when or how Professor Tuckerman became a botanist. But at an early period he was intimate with Dr. Harris, then University Librarian, and with the ardent William Oakes of Ipswich, upon whom, through Dr. Osgood of Danvers, descended the mantle of Manasseh Cutler, of Essex County, the earliest New England botanist.

He must have been attracted to the Lichens almost from the beginning. For his first publications were upon Lichens of New England, largely those of his own collecting in the White and Green Mountains, in two papers, one communicated to the Boston Natural History Society in 1838 or 1839, the other in 1840. These were soon followed by papers on phænogamous botany, viz. one "*On Oakesia*, a new Genus of the Order *Empetreae*," a contribution made while he

was abroad, in the summer of 1842, to Hooker's London Journal of Botany. Unfortunately, the interesting plant which he thus dedicated to his botanical associate, William Oakes, who well deserved such commemoration, proved to be a second species of *Corema*. In 1843, at Schenectady, he privately printed and issued his "Enumeratio Methodica Caricum quarundam," (pp. 21, 8vo,) in which he displayed not only his critical knowledge of the large and difficult genus *Carex*, but also his genius as a systematizer; for this essay was the first considerable, and a really successful, attempt to combine the species of this genus into natural groups. It is wholly in Latin, which he much affected for scientific disquisition as well as for technical characters, and used with facility and elegance. In the same year also appeared, in the American Journal of Science, the first of his "Observations on some interesting Plants of New England." This was followed in 1848 by a second, and in 1849 by a third paper in the same Journal; these containing, *inter alia*, his elaboration of our species of *Potamogeton*, then for the first time critically studied. These papers — with one or two in Hovey's Magazine and elsewhere, at about the same date — may be said to have ended his work in phænogamous botany, although his interest in the subject never died out. For when he accepted the chair of Botany at Amherst he began the preparation of "A Catalogue of Plants growing without Cultivation within thirty Miles of Amherst College," which he published in the year 1875, the late Mr. Charles Frost of Brattleborough contributing the lower Cryptogamia other than the Lichens. In matter and form, as well as in typography (in which Professor Tuckerman had exquisite taste), this catalogue is one of the very best.

But it was to Lichenology that his strength, as indeed almost his whole life, was most assiduously devoted. When, in his youth, the active members of the newly organized Natural History Society of Boston divided among themselves the work of making better known the animals, plants, and minerals of Massachusetts, the study of the Lichens either was assigned to him or he volunteered to undertake it. From this came those earliest papers which have already been mentioned. Also his "Synopsis of the Lichens of New England, the other Northern States, and British America," communicated to this Academy in the autumn of 1847, which is the most considerable botanical contribution to the first volume of the Proceedings. The fourth, fifth, sixth, and seventh volumes contain other of his lichenological papers, of wholly original matter and critical character, — largely upon collections which had begun to come to him from the Rocky Mountain

region, from Texas, the Pacific Coast, the Sandwich Islands, and especially from the rich materials gathered in Cuba and elsewhere by the late Charles Wright. In these years, too, he much helped the study of his favorite plants by the preparation and issue of his "*Lichenes Americae Septentrionalis Exsiccati*," in six fasciculi, or three volumes, highly valued by those who fortunately possess them. Equally fortunate are the herbaria which possess the "*Caroli Wrightii Lichenes Cubae curante E. Tuckerman*," which authenticate his thorough work upon that portion of Mr. Wright's Cuban collections that he undertook to elaborate.

Passing without notice various subsidiary contributions both to journals and to the Reports of Exploring Expeditions, (which, however, are all enumerated in the appended list,) we come to a pamphlet which he independently published at Amherst, in 1866, entitled "*Lichens of California, Oregon, and the Rocky Mountains, so far as yet known*," which, small though it be (pp. 35, 8vo), is particularly noteworthy. For in this he lays down the principles and matured opinions which he had adopted, and which he firmly adhered to, for the taxonomy and classification of Lichens. Those are fully exemplified in the two systematic works to which Professor Tuckerman's later years and maturest powers were persistently devoted, — works which, partly from their publication somewhat out of the ordinary channels, are by no means so well known as they should be, but which surely secure to their author the position of a master in his department, — in which, indeed, we suppose he has left behind him no superior. These works are, first, the "*Genera Lichenum, an Arrangement of the North American Lichens*," (pp. 283, 8vo,) published at Amherst in the year 1872; second, the "*Synopsis of the North American Lichens*," Part I., comprising the *Parmeliacei*, *Cladoniei*, and *Cænogoniei*, published in Boston (by Cassino & Co.) in 1882. It is hoped, but it is not yet certain, that some portions of the remainder, relating to the less conspicuous but more difficult tribes, may have been substantially made ready for the printer. The loss, we fear, is irreparable; for the work cannot be completed by other hands upon quite the same lines, nor in our day with the same knowledge and insight; and Professor Tuckerman's mode of exposition is inimitable.

That which Professor Tuckerman did accomplish, however, suffices to show the wide reach and remarkable precision of his knowledge, his patience and thoroughness in investigation, his sagacity in detecting affinities, and his philosophical and rather peculiar turn of mind. He wrote in a style which — though perhaps founded on that of his

botanical model, Fries, for succinctness, and that of his favorite German philosophical masters for involution — was yet all his own, and which was the more pronounced in advancing years, when, owing to increasing deafness and delicate health, he led a more secluded life. In disquisition, the long and comprehensive sentences which he so carefully constructs are unmistakably clear to those who will patiently plod their way through them, and his choice even of unusual words is generally felicitous; but sometimes the statements are so hedged about and interpenetrated by qualifications or reservations, and so pregnant with subsidiary although relevant considerations, that they are far from easy reading. Like nests of pill-boxes, they are packed into least bulk; but for practical use they need to be taken apart.

That Professor Tuckerman could write idiomatic and clear-flowing English upon occasion, the delightful introduction to his edition of Josselyn's "New England's Rarities" demonstrates; and in the framing of botanical descriptive phrases, Latin or English, in which clearness and brevity with just order and proportion are desiderata, he had hardly a superior.

As has been said, his botanical model was Elias Fries. He had visited him at Upsal, and he kept up a correspondence with him to the end of the venerable botanist's life. He caught from Fries, or he developed independently, and cultivated to perfection, that sense of the value of the indefinable something which botanists inadequately express by the term "habit," which often enables the systematist to *divine* much further than he can perceive in the tracing of relationships. Upon this, in direct reference to Fries, and with a use of the term that seems to correlate it with "insight," Tuckerman remarks: "So great is the value of Habit in minds fully qualified to apprehend and appreciate its subtleties, that such minds may not only anticipate what the microscope is to reveal, but help us to understand its revelations." It should be remembered, however, that when Fries did the best of his work there were no microscopes of much account; and it is probable that Tuckerman would have done more, and perhaps have reached some different conclusions, if he had earlier and more largely used the best instrumental appliances of the time. One advantage, however, of his way of study, and his philosophical conception of an ideal connection of forms which are capable of a wide play of variation, was that he took broad views of genera and species. So he was quite unlike that numerous race of specialists who, in place of characterizing species, describe specimens, and to whom "genus" means the lowest recognizable group of species.

As to the vexed question in Lichenology, which came to him rather late and seemed to threaten the stability of his work, it was most natural that, at his time of life, he did not take kindly to the algo-fungal notion of Lichens, and that he was convinced of its falsity by questionable evidence.

Professor Tuckerman was much more than an excellent specialist. Happily, he did not become such until he had laid a good foundation, for the time, in general systematic botany; and his early studies show that he was a man of scholarly culture over an unusually wide range. He was at home in the leading modern languages; he wrote Latin with reasonable facility, and botanical Latin remarkably well; he had given serious attention to law, divinity, philosophy, and history; and he was fond of antiquarian and genealogical researches. He privately published (without date) a handsome edition of Josselyn's "New England's Rarities Discovered," with copious critical annotations, of 134 pages, including an introduction of 27 pages, which contains a biography of Josselyn, and a sketch of the earlier sources of our knowledge of New England plants and of some of the people who made them known.\* Among them is a biographical notice of Manasseh Cutler, one of the very first elected Fellows of this Academy, the earliest botanical contributor to its Memoirs, — pastor, naturalist, and statesman, the builder of New England in Ohio, probably the originator of the Dane Resolutions in Congress, — a man whose name deserves larger remembrance than it has yet received.

Professor Tuckerman was elected into this Academy in May, 1845. He was one of the corporate members of the National Academy of Sciences at Washington, and has been chosen into several of the learned societies and academies of Europe. He was still young when Nuttall dedicated to him the genus *Tuckermania*, founded upon one of the handsomer of Californian Compositæ, which holds as a subgenus. For one who did not attain the age of sixty-seven, his publications span a remarkably wide interval. It is said that he contributed several short articles on antiquarian topics to the Mercantile Journal in the year 1832. Also that, in 1832 and 1833, he assisted the late Mr. Samuel G. Drake in the preparation of his "Book of the Indians" and "Indian Wars." Then, between 1834 and 1841, he contributed to the New York Churchman no less than fifty-four articles, under the titles of "Notitia Literaria" and "Adversaria," upon points in his-

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\* It appears that this was a contribution to the fourth volume of the *Archæologia Americana*, published in 1860.

tory, biography, and theology. His latest botanical article was contributed to the Bulletin of the Torrey Botanical Club, in 1884. A little later, possibly, are some of his contributions to the Church Eclectic, mostly pseudonymous, — critical notices of recent theological works. He was a keen critic, and very independent in his judgments. He had sounded in his time the depth of various opinions. But as he was born into, so he died, as he had lived, devoutly, in the communion of the Protestant Episcopal Church. With some interruptions, and of late under increasing infirmities, he yet continued his lichenological studies until within a few weeks before the end. Living for a long while in comparative seclusion, few of our younger botanists can have known him personally, or much by correspondence; and most of his old associates and near friends, who knew him best and prized him highly for his sterling character, have gone before him.

*List of the Botanical Publications of EDWARD TUCKERMAN.*

- An Enumeration of some Lichenes of New England, with Remarks. (Boston Journ. of Nat. Hist., Vol. II., 1838-39, pp. 245-262.)
- A Further Enumeration of some New England Lichenes. (Boston Journ. of Nat. Hist., Vol. III., 1840-41, pp. 281-306 and 438-464.)
- A Further Enumeration of some Alpine and other Lichenes of New England. (Boston Journ. of Nat. Hist., Vol. V., 1845-47, pp. 93-104.)
- On Oakesia, a new Genus of the Order Empetrea. (Hooker's London Journ. of Botany, Vol. I., 1842, pp. 443-447.)
- Enumeratio Methodica Caricum quarundam: Species recensuit et secundum habitum pro viribus disponere tentavit. Schenectadiæ, 1843, pp. 21.
- Observations on some interesting Plants of New England. (Amer. Journ. of Science, Vol. XLV., 1843, pp. 27-49.)
- A Synopsis of the Lichenes of the Northern United States and British America. (Proc. Amer. Acad., Vol. I., 1846-48, pp. 195-285.)
- Notice of some Cyperaceæ of our Vicinity. (Hovey's Mag. of Hort. and Bot., Vol. VII., 1841, pp. 208-210.)
- Description of several New Plants of New England. (Hovey's Mag. of Hort., Vol. IX., 1843, pp. 142-145.)
- Observations on some New England Plants, with Characters of several new Species. (Amer. Journ. of Science, Vol. VI., 1848, pp. 224-232.)
- Observations on some American Species of the Genus Potamogeton, L. (Amer. Journ. of Science, Vol. VII., 1849, pp. 347-360.)
- Lichenes Americæ Septentrionalis Exsiccati, Fascic. I., II., Cantab., 1847, pp. 50. Fascic. III., IV., Bost., 1854, pp. 50. Fascic. V., VI., Bost., 1855, pp. 50.
- The Lichenes of Lea's Catalogue of the Plants of Cincinnati, Ohio. Phila., 1849, pp. 44-47.
- Observations on North American and some other Lichenes. (Proc. Amer. Acad., Vol. IV., 1857-60, pp. 383-407.)
- Supplement to an Enumeration of North American Lichenes, containing brief

- Diagnoses of New Species. (Amer. Journ. of Science, Vol. XXV., 1858, pp. 422-430.)
- Supplement to an Enumeration of North American Lichenes, containing brief Diagnoses of New Species. (Amer. Journ. of Science, Vol. XXVIII., 1859, pp. 200-206.)
- Carex argyrantha* *sp. nov.*, distributed from Amherst, 1859, published in Wood's Class-Book of Botany, 1861, p. 753.
- Observations on North American and other Lichenes. (Proc. Amer. Acad., Vol. V., 1860-62, pp. 383-422.)
- Observations on North American and other Lichenes. (Proc. Amer. Acad., Vol. VI., 1862-65, pp. 263-287.)
- Lichens of the Hawaiian Islands. (Proc. Amer. Acad., Vol. VII., 1865-68, pp. 223-235.)
- Lichens of California, Oregon, and the Rocky Mountains; so far as yet known. With an Appendix. Amherst, 1866, pp. 35.
- Carex glaucoidea*. (Proc. Amer. Acad., Vol. VII., 1865-68, p. 395.)
- Can Lichens be identified by Chemical Tests? (Amer. Naturalist, Vol. II., 1868, pp. 104-107.)
- Lichenes. (From the Botany of the U. S. Exploring Expedition under Captain Wilkes.) Vol. XVII., 1874, pp. 113-152. (A few copies of these pages had been previously issued in 1862.)
- Two Lichens of Oregon. (Bulletin of the Torrey Bot. Club, Vol. V., 1874, p. 20.)
- Lecidea elabens*, Th. Fr. Lich. Scand., p. 554. (Flora, 1875, p. 65.)
- Lichens of Kerguelen's Land. (Bulletin of the Torrey Bot. Club, Vol. VI., 1875, pp. 57-59; also National Museum, Bulletin No. 3, 1876, pp. 27-30.)
- Observationes Lichenologicæ. Observations on North American and other Lichens. (Proc. Amer. Acad., Vol. XII., 1876-79, pp. 166-185.)
- Lichens of Arctic America. (National Museum, Bulletin No. 15, Washington, 1879, pp. 167, 168.)
- The Question of the Gonidia of Lichens. (Amer. Journ. of Science, Vol. XVII. 1879, pp. 254-256.)
- Lichenes. U. S. Geographical Surveys West of the 100th Meridian, Vol. VI., 1878, pp. 350, 351.
- Lichens or Fungi? (Bulletin Torrey Bot. Club, Vol. VIII., 1881, pp. 66, 67.)
- Review of Symbolæ Licheno-Mycologicæ. (Bulletin Torrey Bot. Club, Vol. IX., 1882, p. 143.)
- A New *Ramalina* (*crinita*). (Bulletin Torrey Bot. Club, Vol. X., 1883, p. 43.)
- New Western Lichens. (Bulletin Torrey Bot. Club, Vol. X., 1883, pp. 21, 22.)
- Two Lichens of the Pacific Coast. (Bulletin Torrey Bot. Club, Vol. XI., 1884, pp. 25, 26.)
- An Enumeration of North American Lichenes, etc. Cambridge, 1845, pp. 65.
- A Synopsis of the Lichenes of New England, the other Northern States, and British America. Cambridge, 1848. (Proc. Amer. Acad., Vol. I., pp. 93.)
- Genera Lichenum: An Arrangement of the North American Lichens. Amherst, 1872, pp. 281.
- A Catalogue of Plants growing without Cultivation within thirty Miles of Amherst College. Amherst, 1875, pp. 98.
- A Synopsis of the North American Lichens. Part I. Boston, 1882, pp. 261.

Contributed the chapters on Exploration and Botany to T. Starr King's "White Hills of New Hampshire," 1859.

Edited, with an Introduction and Notes, "New England's Rarities Discovered," by John Josselyn. (*Archæologia Americana*, Vol. IV., 1860, pp. 134.)

Contributed to Agassiz's Account of a Journey to Lake Superior, etc. Boston, 1850, pp. 170-174.

Contributed the articles on Lichenes to the Pacific Railroad Reports of Explorations and Surveys, Vol. VI., 1857, p. 94; and to King's Report of Geological Exploration along the 40th Parallel, Vol. V., 1871, pp. 412, 413.

## FOREIGN HONORARY MEMBERS.

### HENRI MILNE EDWARDS.

HENRI MILNE EDWARDS died at Paris, July 29, 1885, at the age of eighty-five. Born in Belgium, he took his diploma in medicine in Paris, but devoted himself directly to scientific researches among the invertebrate animals. Paris was then the centre of the world for zoölogical studies, with Cuvier, Lamarck, Latreille, Geoffroy Saint-Hilaire, Dumeril, and many others. Milne Edwards was among the first who, not content with the study of the dead forms of animal life, made prolonged visits to the sea-coasts to study the living forms and to investigate their habits. Among his very numerous publications, his "*Histoire Naturelle des Crustacés*," 1834-40, a work in which he was associated with his friend Victor Audouin, remained long as a standard authority on this group of animals. His "*Leçons sur la Physiologie et l'Anatomie comparée de l'Homme et des Animaux*," 1857-81, in fourteen volumes, is also an important work to the student from the immense mass of details and references which it contains. The editorship of the zoölogical portion of the "*Annales des Sciences Naturelles*" was for fifty years in his hands. He was Professor of Entomology, later Professor of Zoölogy, at the Museum of the Jardin des Plantes, and later Assistant Director of the Museum. Milne Edwards's study of the geographical distribution of the lower forms of Invertebrates — then a nearly new field — led him to the theory of definite centres of creation. Therefore he has never accepted Darwin's theory. Milne Edwards will always rank high among the naturalists of this century; he was through more than half of its course a most reliable, most industrious, and most indefatigable worker. He was kindly and affable to all; and his house at the Jardin des Plantes was for many years the focus of attraction for all the men of science in or visiting Paris.

## CARL THEODOR ERNST VON SIEBOLD.

CARL THEODOR ERNST VON SIEBOLD, the last in the male line of a family very distinguished during four generations in science and medicine, was born in Würzburg, Germany, on the 16th of February, 1804. After a long career of almost incessant and invariably successful industry, his life closed on the 7th of April, 1885, at Munich. His death deprives the Academy, of which he became an honorary member in 1854, of one of its most distinguished associates.

Siebold was a zoölogist from inward necessity, and turned to zoölogy as an occupation under all circumstances. He had a natural inclination for collecting and systematic arrangement, and an irrepressible interest in the living animal. These two tastes were his most marked professional traits, and fixed to a great extent the scope of his work. His researches were in large part, though not exclusively, upon the species and classification of various groups, and secondly upon the phenomena of animal reproduction. The former class of investigations reveal the painstaking and accurate temperament of the man, and also his extensive knowledge of the literature of his science. They are represented by numerous papers on Invertebrates, and an invaluable monograph of the Fresh-water Fishes of Middle Germany, — a work undertaken at royal request, and representing the labor of several years. His most important achievement in systematic zoölogy was the definite recognition of the protozoa as unicellular animals, forming a distinct sub-kingdom. This fine generalization has been the basis of all the subsequent progress of knowledge concerning this group.

Siebold's studies upon reproduction were very fruitful, and their fruit of the best value. He elucidated much of our present knowledge of the life history of helminths, a subject of equal scientific and practical importance; and it is principally to his many observations that we owe the discovery of the laws of parthenogenesis, one of the most significant phenomena of animal life.

Besides all this, Von Siebold produced, together with Stannius, a text-book of Comparative Anatomy, which, though written forty years ago, has never been surpassed in thoroughness and comprehensive treatment, and still remains a mine of information to the student. This remarkable book, of which Siebold wrote the part dealing with the Invertebrates, is not a mere compilation, although it shows an exhaustive acquaintance with the literature of the subjects, but is much more, since it contains very numerous original observations.

We must also mention the gathering of Siebold's large collection of helminths which is now in the Museum at Moscow, and his gradual extension and perfection of the zoölogical collections at Munich, of which he had charge for some thirty years.

Von Siebold was educated as a physician, and began practice as a "Kreisphysicus" at Heilsperg, Prussia, and subsequently continued it as director of a lying-in hospital at Danzig. In 1840 he was called to Erlangen as full Professor of Zoölogy, Comparative Anatomy, and Veterinary Medicine; in 1845 he changed to the University at Freiburg; in 1850, to Breslau; in 1853, to Munich, where he remained until his death, continuing his active teaching until 1883. He married Fanny Nöldechen in 1830, and a year after her death married, in 1855, her sister. It is noteworthy that his academical career did not begin until he was thirty-six.

He was a large man, whose hair early turned gray, and whose short-sighted eyes were shadowed by heavy eyebrows. He was genial with his students and much liked by them, though less excellent in the lecture-room than in personal intercourse. He was devoted to music, which was his constant solace and of which he possessed much knowledge.

Siebold is most widely known as the founder of the "Zeitschrift für wissenschaftliche Zoologie," which was inaugurated in 1849, and has now passed its fortieth volume. Probably no other periodical has exercised as great an influence as this Zeitschrift in furthering the highest interests of that science to which Von Siebold devoted the best powers of his long and honored life.

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Since the last Report, the Academy has received an accession of ten new members; viz. three Resident Fellows, four Associate Fellows, and three Foreign Honorary Members. The list of the Academy, corrected to the date of this Report, is hereto added. It includes 192 Resident Fellows, 88 Associate Fellows, and 72 Foreign Honorary Members.



# LIST

OF THE FELLOWS AND FOREIGN HONORARY MEMBERS.

## RESIDENT FELLOWS.—192.

(Number limited to two hundred.)

### CLASS I.—*Mathematical and Physical Sciences.*—78.

#### SECTION I.—7.

##### *Mathematics.*

Benjamin A. Gould,	Cambridge.
Gustavus Hay,	Boston.
Benjamin O. Peirce,	Cambridge.
James M. Peirce,	Cambridge.
John D. Runkle,	Brookline.
Edwin P. Seaver,	Newton.
T. H. Safford,	Williamstown.

#### SECTION II.—14.

##### *Practical Astronomy and Geodesy.*

J. Ingersoll Bowditch,	Boston.
Seth C. Chandler, Jr.,	Cambridge.
Alvan Clark,	Cambridgeport.
Alvan G. Clark,	Cambridgeport.
George B. Clark,	Cambridgeport.
J. Rayner Edmands,	Cambridge.
Henry Mitchell,	Boston.
Edward C. Pickering,	Cambridge.
William A. Rogers,	Cambridge.
Edwin F. Sawyer,	Cambridge.
Arthur Searle,	Cambridge.
Leopold Trouvelot,	Cambridge.
O. C. Wendell,	Cambridge.
Henry L. Whiting,	Tisbury.

#### SECTION III.—42.

##### *Physics and Chemistry.*

A. Graham Bell,	Cambridge.
Clarence J. Blake,	Boston.
Francis Blake,	Weston.
John H. Blake,	Boston.
Thos. Edwards Clark,	Williamstown.
Josiah P. Cooke,	Cambridge.

James M. Crafts,	Boston.
Charles R. Cross,	Boston.
William P. Dexter,	Roxbury.
Amos E. Dolbear,	Somerville.
Charles W. Eliot,	Cambridge.
Moses G. Farmer,	New York.
Thomas Gaffield,	Boston.
Wolcott Gibbs,	Cambridge.
Frank A. Gooch,	Cambridge.
Edwin H. Hall,	Cambridge.
Henry B. Hill,	Cambridge.
N. D. C. Hodges,	Salem.
Silas W. Holman,	Boston.
William L. Hooper,	Somerville.
Eben N. Horsford,	Cambridge.
T. Sterry Hunt,	Montreal.
Charles L. Jackson,	Cambridge.
William W. Jacques,	Newtonville.
Alonzo S. Kimball,	Worcester.
Leonard P. Kinnicutt,	Worcester.
Joseph Lovering,	Cambridge.
Charles F. Mabery,	Cambridge.
Alfred Michael,	Medford.
William R. Nichols,	Boston.
Lewis M. Norton,	Newton.
John M. Ordway,	Boston.
William H. Pickering,	Boston.
Robert H. Richards,	Boston.
Edward S. Ritchie,	Brookline.
Stephen P. Sharples,	Cambridge.
Francis H. Storer,	Boston.
John Trowbridge,	Cambridge.
Cyrus M. Warren,	Brookline.
Harold Whiting,	Cambridge.
Charles H. Wing,	Boston.
Edward S. Wood,	Cambridge.

## SECTION IV. — 15.

*Technology and Engineering.*

George R. Baldwin, Woburn.  
 John M. Batchelder, Cambridge.  
 Chas. O. Boutelle, Washington, D.C.  
 James B. Francis, Lowell.  
 John B. Henck, Boston.  
 Gaetano Lanza, Boston.

E. D. Leavitt, Jr., Cambridge.  
 William R. Lee, Roxbury.  
 Frederic W. Lincoln, Boston.  
 Hiram F. Mills, Lawrence.  
 Alfred P. Rockwell, Boston.  
 Charles S. Storrow, Boston.  
 William R. Ware, New York.  
 William Watson, Boston.  
 Morrill Wyman, Cambridge.

CLASS II. — *Natural and Physiological Sciences.* — 56.

## SECTION I. — 8.

*Geology, Mineralogy, and Physics of the Globe.*

Thomas T. Bouvé, Boston.  
 William T. Brigham, Boston.  
 Algernon Coolidge, Boston.  
 William O. Crosby, Boston.  
 William M. Davis, Cambridge.  
 Jules Marcou, Cambridge.  
 William H. Niles, Cambridge.  
 Nathaniel S. Shaler, Cambridge.

Edward Burgess, Boston.  
 John Dean, Waltham.  
 Walter Faxon, Cambridge.  
 Hermann A. Hagen, Cambridge.  
 Alpheus Hyatt, Cambridge.  
 Samuel Kneeland, Boston.  
 Theodore Lyman, Brookline.  
 Edward L. Mark, Cambridge.  
 Charles S. Minot, Boston.  
 Edward S. Morse, Salem.  
 James J. Putnam, Boston.  
 Samuel H. Scudder, Cambridge.  
 William T. Sedgwick, Boston.  
 D. Humphreys Storer, Boston.  
 Henry Wheatland, Salem.  
 James C. White, Boston.

## SECTION II. — 7.

*Botany.*

William G. Farlow, Cambridge.  
 George L. Goodale, Cambridge.  
 Asa Gray, Cambridge.  
 H. H. Hunnewell, Wellesley.  
 Charles S. Sargent, Brookline.  
 Charles J. Sprague, Boston.  
 Sereno Watson, Cambridge.

## SECTION IV. — 19.

*Medicine and Surgery.*

## SECTION III. — 22.

*Zoölogy and Physiology.*

Alex. E. R. Agassiz, Cambridge.  
 Joel A. Allen, New York.  
 Robert Amory, Brookline.  
 Nath. E. Atwood, Provincetown.  
 James M. Barnard, Boston.  
 Henry P. Bowditch, Boston.

Samuel L. Abbot, Boston.  
 Henry J. Bigelow, Boston.  
 Henry I. Bowditch, Boston.  
 Benjamin E. Cotting, Roxbury.  
 Frank W. Draper, Boston.  
 Thomas Dwight, Boston.  
 Robert T. Edes, Boston.  
 Charles F. Folsom, Boston.  
 Richard M. Hodges, Boston.  
 Oliver W. Holmes, Boston.  
 Alfred Hosmer, Watertown.  
 Francis Minot, Boston.  
 John P. Reynolds, Boston.

Wm. L. Richardson, Boston.  
George C. Shattuck, Boston.  
J. Baxter Upham, Boston.

Charles E. Ware, Boston.  
John C. Warren, Boston.  
Henry W. Williams, Boston.

CLASS III. — *Moral and Political Sciences.* — 58.

SECTION I. — 14.

*Philosophy and Jurisprudence.*

James B. Ames, Cambridge.  
Charles S. Bradley, Providence.  
Phillips Brooks, Boston.  
James F. Clarke, Jamaica Pl.  
Charles C. Everett, Cambridge.  
Horace Gray, Boston.  
John C. Gray, Boston.  
Laurens P. Hickock, Northampton.  
Oliver W. Holmes, Jr., Boston.  
Mark Hopkins, Williamstown.  
C. C. Langdell, Cambridge.  
John Lowell, Newton.  
Henry W. Paine, Cambridge.  
James B. Thayer, Cambridge.

SECTION II. — 15.

*Philology and Archæology.*

William S. Appleton, Boston.  
William P. Atkinson, Boston.  
Lucien Carr, Boston.  
Joseph T. Clarke, Boston.  
Henry G. Denny, Boston.  
Epes S. Dixwell, Cambridge.  
William Everett, Quincy.  
William W. Goodwin, Cambridge.  
Ephraim W. Gurney, Cambridge.  
Henry W. Haynes, Boston.  
Bennett H. Nash, Boston.  
Frederick W. Putnam, Cambridge.  
John W. White, Cambridge.  
Justin Winsor, Cambridge.  
Edward J. Young, Cambridge.

SECTION III. — 19.

*Political Economy and History.*

Chas. F. Adams, Jr., Quincy.  
Henry Adams, Washington.  
Edward Atkinson, Boston.  
John Cummings, Woburn.  
Charles Deane, Cambridge.  
Charles F. Dunbar, Cambridge.  
Samuel Eliot, Boston.  
George E. Ellis, Boston.  
Edwin L. Godkin, New York.  
Edward Everett Hale, Boston.  
Henry C. Lodge, Boston.  
Augustus Lowell, Boston.  
Francis Parkman, Boston.  
Andrew P. Peabody, Cambridge.  
John C. Ropes, Boston.  
Denman W. Ross, Cambridge.  
Henry W. Torrey, Cambridge.  
Francis A. Walker, Boston.  
Robert C. Winthrop, Boston.

SECTION IV. — 10.

*Literature and the Fine Arts.*

Charles F. Adams, Boston.  
George S. Boutwell, Groton.  
J. Elliot Cabot, Brookline.  
Francis J. Child, Cambridge.  
Charles G. Loring, Boston.  
James Russell Lowell, Cambridge.  
Charles Eliot Norton, Cambridge.  
Thomas W. Parsons, Boston.  
Charles C. Perkins, Boston.  
John G. Whittier, Amesbury.

## ASSOCIATE FELLOWS. — 88.

(Number limited to one hundred.)

CLASS I. — *Mathematical and Physical Sciences.* — 35.

## SECTION I. — 6.

*Mathematics.*

E. B. Elliott, Washington, D.C.  
 William Ferrel, Washington, D.C.  
 Thomas Hill, Portland, Me.  
 Simon Newcomb, Washington, D.C.  
 H. A. Newton, New Haven, Conn.  
 James E. Oliver, Ithaca, N.Y.

## SECTION II. — 13.

*Practical Astronomy and Geodesy.*

W. H. C. Bartlett, Yonkers, N.Y.  
 J. H. C. Coffin, Washington, D.C.  
 Wm. H. Emory, Washington, D.C.  
 Asaph Hall, Washington, D.C.  
 J. E. Hilgard, Washington, D.C.  
 George W. Hill, Nyack, N.Y.  
 E. S. Holden, Madison, Wis.  
 Sam. P. Langley, Allegheny, Pa.  
 Elias Loomis, New Haven, Conn.  
 Maria Mitchell, Poughkeepsie, N.Y.  
 C. H. F. Peters, Clinton, N.Y.

George M. Searle, New York.  
 Chas. A. Young, Princeton, N.J.

## SECTION III. — 10.

*Physics and Chemistry.*

F. A. P. Barnard, New York.  
 J. Willard Gibbs, New Haven, Conn.  
 S. W. Johnson, New Haven, Conn.  
 John Le Conte, Berkeley, Cal.  
 J. W. Mallet, Charlottesville, Va.  
 A. M. Mayer, Hoboken, N. J.  
 Albert A. Michelson, Cleveland, O.  
 Ogden N. Rood, New York.  
 H. A. Rowland, Baltimore.  
 L. M. Rutherford, New York.

## SECTION IV. — 6.

*Technology and Engineering.*

Henry L. Abbot, New York.  
 Geo. W. Cullum, New York.  
 Geo. S. Morison, New York.  
 William Sellers, Philadelphia.  
 George Talcott, Albany, N.Y.  
 W. P. Trowbridge, New Haven, Conn.

CLASS II. — *Natural and Physiological Sciences.* — 26.

## SECTION I. — 13.

*Geology, Mineralogy, and Physics of the Globe.*

Cleveland Abbe, Washington, D.C.  
 George J. Brush, New Haven, Conn.  
 James D. Dana, New Haven, Conn.  
 J. W. Dawson, Montreal, Canada.  
 J. C. Fremont, New York.

F. A. Genth, Philadelphia.  
 James Hall, Albany, N.Y.  
 F. S. Holmes, Charleston, S.C.  
 Clarence King, Washington, D.C.  
 Joseph Le Conte, Berkeley, Cal.  
 J. Peter Lesley, Philadelphia.  
 R. Pumpelly, Newport, R.I.  
 Geo. C. Swallow, Columbia, Mo.

## SECTION II. — 2.

*Botany.*

A. W. Chapman, Apalachicola, Fla.  
 Leo Lesquereux, Columbus, Ohio.

## SECTION III. — 6.

*Zoölogy and Physiology.*

S. F. Baird, Washington, D.C.  
 J. C. Dalton, New York.  
 Joseph Leidy, Philadelphia.

O. C. Marsh, New Haven, Conn.  
 S. Weir Mitchell, Philadelphia.  
 A. S. Packard, Providence.

## SECTION IV. — 5.

*Medicine and Surgery.*

Fordyce Barker, New York.  
 John S. Billings, Washington, D.C.  
 Jacob M. Da Costa, Philadelphia.  
 W. A. Hammond, New York.  
 Alfred Stillé, Philadelphia.

CLASS III. — *Moral and Political Sciences.* — 27.

## SECTION I. — 9.

*Philosophy and Jurisprudence.*

D. R. Goodwin, Philadelphia.  
 A. G. Haygood, Oxford, Ga.  
 R. G. Hazard, Peacedale, R.I.  
 Nathaniel Holmes, Cambridge.  
 James McCosh, Princeton, N.J.  
 Charles S. Peirce, New York.  
 Noah Porter, New Haven, Conn.  
 E. G. Robinson, Providence.  
 Jeremiah Smith, Dover, N.H.

W. D. Whitney, New Haven, Conn.  
 T. D. Woolsey, New Haven, Conn.

## SECTION III. — 6.

*Political Economy and History.*

George Bancroft, Washington, D.C.  
 S. G. Brown, Hanover, N.H.  
 Henry C. Lea, Philadelphia.  
 J. H. Trumbull, Hartford, Conn.  
 M. F. Force, Cincinnati.  
 W. G. Sumner, New Haven, Conn.

## SECTION II. — 7.

*Philology and Archæology.*

A. N. Arnold, Pawtuxet, R.I.  
 D. C. Gilman, Baltimore.  
 A. C. Kendrick, Rochester, N.Y.  
 E. E. Salisbury, New Haven, Conn.  
 A. D. White, Ithaca, N.Y.

## SECTION IV. — 5.

*Literature and the Fine Arts.*

James B. Angell, Ann Arbor, Mich.  
 L. P. di Cesnola, New York.  
 F. E. Church, New York.  
 R. S. Greenough, Florence.  
 William W. Story, Rome.

## FOREIGN HONORARY MEMBERS.—72.

(Appointed as vacancies occur.)

CLASS I.—*Mathematical and Physical Sciences.*—24.

## SECTION I.—6.

*Mathematics.*

John C. Adams,	Cambridge.
Sir George B. Airy,	Greenwich.
Francesco Brioschi,	Milan.
Arthur Cayley,	Cambridge.
Charles Hermite,	Paris.
J. J. Sylvester,	Oxford.

## SECTION II.—5.

*Practical Astronomy and Geodesy.*

Arthur Auwers,	Berlin.
J. H. W. Döllén,	Pulkowa.
H. A. E. A. Faye,	Paris.
Eduard Schönfeld,	Bonn.
Otto Struve,	Pulkowa.

## SECTION III.—10.

*Physics and Chemistry.*

Adolf Baeyer,	Munich.
Marcellin Berthelot,	Paris.
R. Bunsen,	Heidelberg.
M. E. Chevreul,	Paris.
H. Helmholtz,	Berlin.
A. W. Hofmann,	Berlin.
G. Kirchhoff,	Berlin.
Balfour Stewart,	Manchester.
G. G. Stokes,	Cambridge.
Julius Thomsen,	Copenhagen.

## SECTION IV.—3.

*Technology and Engineering.*

R. Clausius,	Bonn.
F. M. de Lesseps,	Paris.
Sir Wm. Thomson,	Glasgow.

CLASS II.—*Natural and Physiological Sciences.*—28.

## SECTION I.—7.

*Geology, Mineralogy, and Physics of the Globe.*

Heinrich E. Beyrich,	Berlin.
Alfred des Cloizeaux,	Paris.
James Prescott Joule,	Manchester.
C F. Rammelsberg,	Berlin.
A. C. Ramsay,	London.
Bernhard Studer,	Berne.
Heinrich Wild,	St. Petersburg.

## SECTION II.—7.

*Botany.*

J. G. Agardh,	Lund.
Alphonse de Candolle,	Geneva.
August W. Eichler,	Berlin.
Sir Joseph D. Hooker,	London.
Carl Nägeli,	Munich.
Julius Sachs,	Würzburg.
Marquis de Saporta,	Aix.

## SECTION III. — 10.

*Zoölogy and Physiology.*

Van Beneden,	Louvain.
Du Bois-Reymond,	Berlin.
Thomas H. Huxley,	London.
Albrecht Kölliker,	Würzburg.
Lacaze-Duthiers,	Paris.
Rudolph Leuckart,	Leipsic.
C. F. W. Ludwig,	Leipsic.
Richard Owen,	London.

Louis Pasteur,	Paris.
J. J. S. Steenstrup,	Copenhagen.

## SECTION IV. — 4.

*Medicine and Surgery.*

C. E. Brown-Séquard,	Paris.
F. C. Donders,	Utrecht.
Sir James Paget,	London.
Robert Virchow,	Berlin.

CLASS III. — *Moral and Political Sciences.* — 20.

## SECTION I. — 3.

*Philosophy and Jurisprudence.*

Sir Henry Sumner Maine,	London.
James Martineau,	London.
Sir James F. Stephen,	London.

## SECTION II. — 7.

*Philology and Archæology.*

Georg Curtius,	Leipsic.
Pascual de Gayangos,	Madrid.
Benjamin Jowett,	Oxford.
G. C. C. Maspero,	Cairo.
Max Müller,	Oxford.
H. A. J. Munro,	Cambridge.
Sir H. C. Rawlinson,	London.

## SECTION III. — 6.

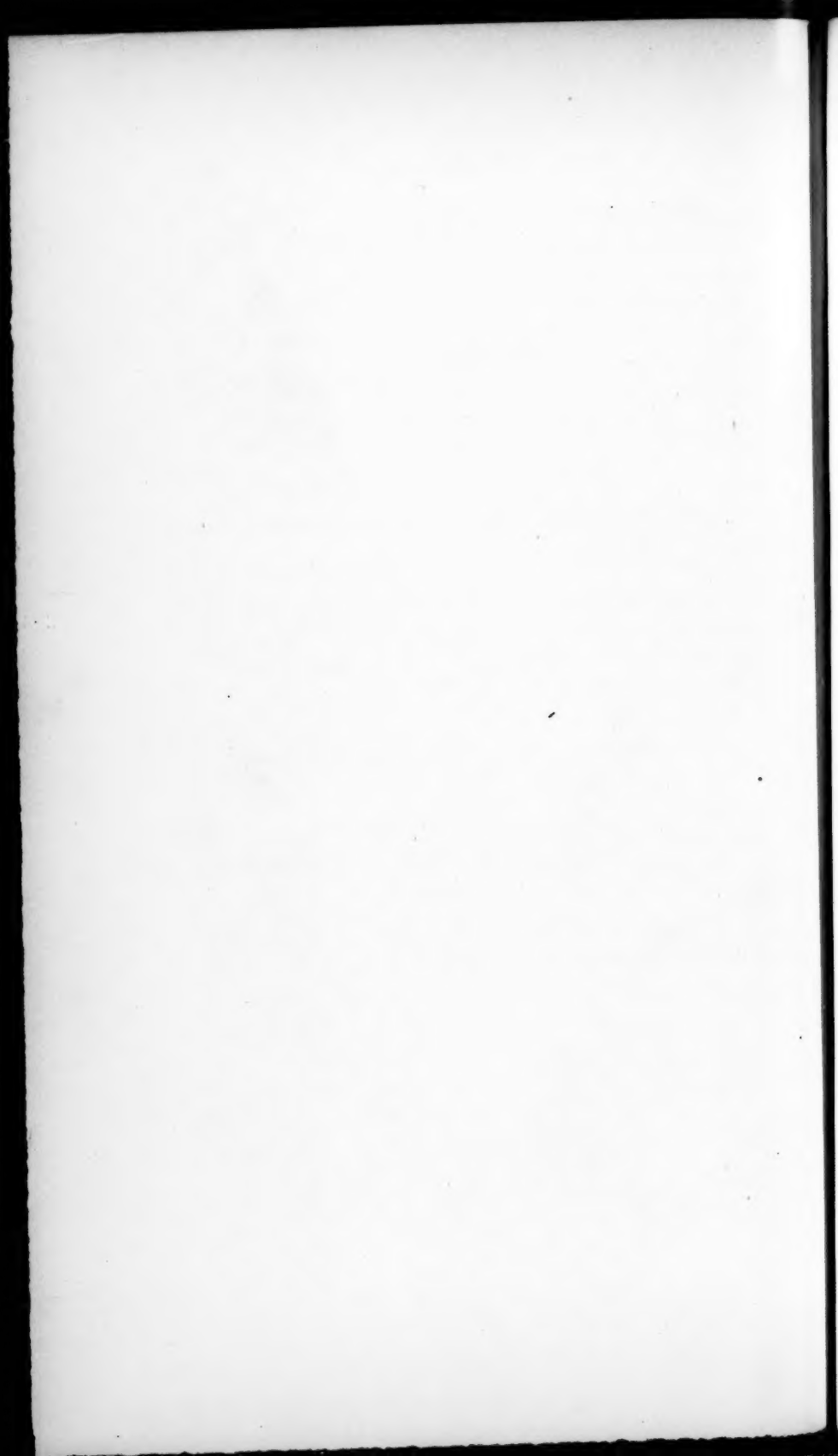
*Political Economy and History.*

Ernst Curtius,	Berlin.
W. Ewart Gladstone,	London.
Charles Merivale,	Ely.
Theodor Mommsen,	Berlin.
Jules Simon,	Paris.
William Stubbs,	Chester.

## SECTION IV. — 4.

*Literature and the Fine Arts.*

Matthew Arnold,	London.
Jean Léon Gérôme,	Paris.
John Ruskin,	Coniston.
Lord Tennyson,	Isle of Wight.



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